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16. Abstracts

Successful carbon monoxide monitoring over long paths ~~is~~ performed during the 1975 Regional Air Pollution Study (RAPS) of the U.S. Environmental Protection Agency. Over 40 days of monitoring ~~are~~ carried out at Regional Air Monitoring Station (RAMS) Sites 108 and 105. These data ~~are~~ analyzed with assigned error bars, and are presented on 24-hour daily plots. Correlations with meteorological data are continuing in order to obtain relevant information for pollution modeling. Some unexpected problems in calibration drift, non-linearity and interference ~~are~~ encountered this year, but they ~~are~~ successfully minimized in the field. As these problems ~~are~~ caused, in part, by use of some of the first commercially-produced diode lasers, they are expected to diminish as more satisfactory manufacturing techniques are developed. In Section 2 of this report, the results and accomplishments of the 1975 RAPS study are summarized. Monitoring data and discussion are presented in Section 3. System accuracy and error analysis are described in Section 4. Conclusions and recommendations for future work are presented in Section 5.

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Long-Path Monitoring of Atmospheric Carbon Monoxide

1975 Regional Air Pollution Study

St. Louis, Missouri

April 1976

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LONG-PATH MONITORING OF ATMOSPHERIC CARBON MONOXIDE

1975 Regional Air Pollution Study, St. Louis, Missouri

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Any opinions, findings, conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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TABLE OF CONTENTS

	Page
1. INTRODUCTION	1
2. SUMMARY OF RAPS-1975 MEASUREMENTS	7
3. RAPS-75 MEASUREMENTS DATA	11
A. RAMS Site 108, Granite City, Illinois 7 July - 4 August 1975	11
B. RAMS Site 105, Downtown St. Louis, Missouri, 6 August - 10 September 1975	19
4. SYSTEM ACCURACY AND DATA ERROR ANALYSIS	26
5. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE MONITORING	31
ACKNOWLEDGMENTS	32
REFERENCES	33
APPENDIX A - 1975 RAPS Measurement Data	35
APPENDIX B - 1974 RAPS Measurement Data	77
APPENDIX C - Long-Path Monitoring of Atmospheric Carbon Monoxide with a Tunable Diode Laser System	107

Long-Path Laser Monitoring of Atmospheric Carbon Monoxide — 1975 Regional Air Pollution Study, St. Louis, Missouri

1. INTRODUCTION

There is an urgent need by the U.S. Environmental Protection Agency as well as several other Federal and local agencies, utilities, and industries (particularly chemical and petroleum) for in-situ monitoring of atmospheric pollutant gases over extended paths. The Environmental Protection Agency has included the long-path laser monitoring techniques in its 5-year comprehensive Regional Air Pollution Study (RAPS) conducted in the St. Louis area. The long-path results will be used to evaluate and help develop several computer models for understanding and forecasting atmospheric pollutant levels.

During the last few years, Lincoln Laboratory has been developing and applying semiconductor diode lasers to pollutant gas detection, with support from the National Science Foundation and the Environmental Protection Agency. The diode lasers were first applied to the detection of ethylene (C_2H_4) and nitric oxide (NO) in automobile exhausts in 1971.[1] Stack monitoring of sulfur dioxide (SO_2) was performed using diode lasers in 1972.[2] In 1973, an ambient monitoring system for carbon monoxide (CO) was developed and utilized to perform measurements over a 0.61-km path.[3,4] The entire system was incorporated into a mobile van and driven to St. Louis for atmospheric CO monitoring in the 1974 RAPS program.[5] The 1974 RAPS accomplishments included validation of the long-path laser technique by comparison with a conventional point sampling instrument, extending the total monitored path length to 2 km, and obtaining data on ambient CO levels over various paths at three different field sites. The 1974 RAPS laser-monitoring results are included in Appendix B of this interim report.

During the period 7 July 1975 to 10 September 1975, the tunable semiconductor diode laser system for long-path monitoring was again stationed

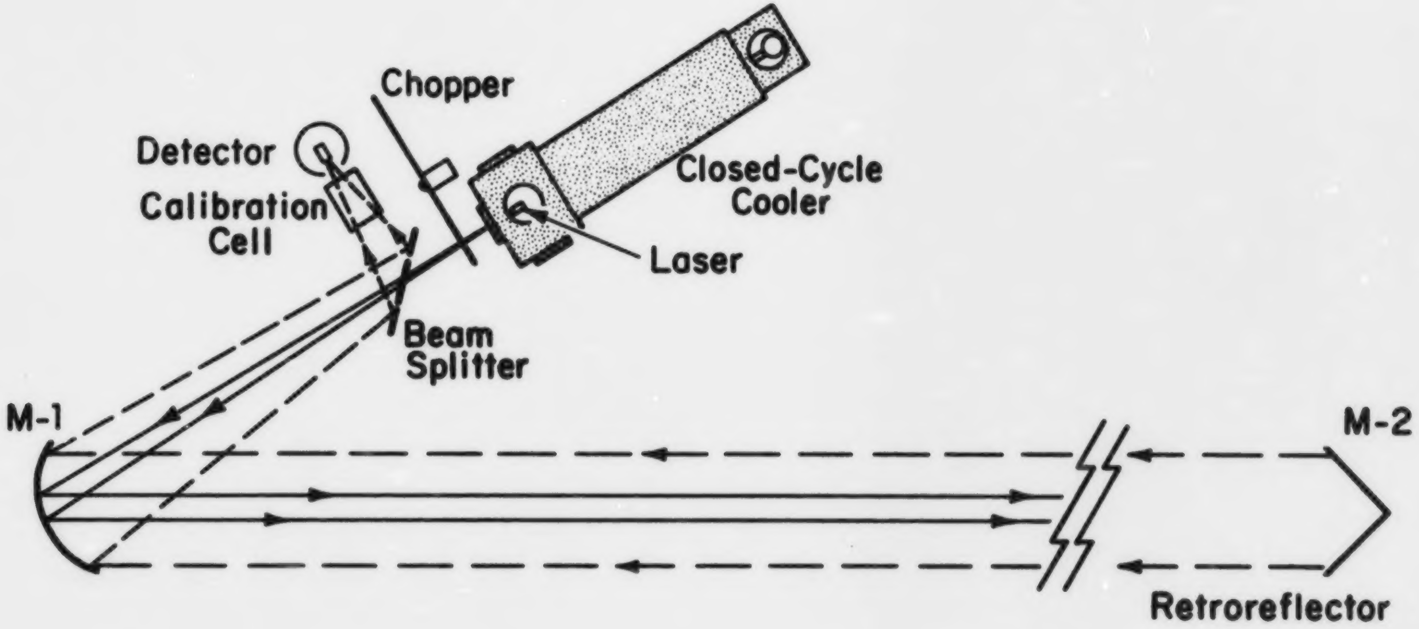

Chopper
Detector
Calibration
Cell
Closed-Cycle
Cooler
Laser
Beam
Splitter
M-1
M-2
Retroreflector

Fig.1. Optical system for long-path laser monitoring.

at St. Louis to participate in the 1975 Regional Air Pollution Study (RAPS-75). The system, housed in a mobile van, was located at Site 108 (on a farm just north of Granite City, Illinois) for the first half of the program to 4 August, and then moved to Site 105 (inner St. Louis) for the duration.

Approximately 40 days of long-path CO monitoring were obtained, including several around-the-clock periods and weekends. A great deal of time was spent this year in validating the calibrations in order to establish quality assurance of the data. Long-path results were compared with RAMS (Regional Air Monitoring Station) readings (validated over hourly periods) and a gas-filter correlation instrument developed by Philco-Ford under another EPA contract.

Before the presentation and discussion of RAPS-75 results, a brief review will be given of the laser measurement and calibration procedures. For a more detailed description, please refer to Appendix C.

Many atmospheric pollutant gases, e.g., NO, C_2H_4, SO_2, CO, O_3 and CO_2, have already been detected by various tunable laser techniques.[6] The semiconductor laser we use is one of the Pb-salt types which have several inherent advantages for field application over other types of tunable lasers: small size, ease in frequency tunability, and low power (eye-safe level) operation. A $PbS_{1-x}Se_x$ ($x = 0.18$) laser is chemically tailored to operate in the 4.7-μm wavelength region in close coincidence with the fundamental vibrational band of CO centered at 2145 cm^{-1}. Exact frequency matching and tuning through CO absorption lines is achieved by varying the injection current, which changes the junction temperature, thus the laser frequency.[1]

The essential components of the laser monitoring system are shown in Fig. 1. The diode laser is mounted inside a closed-cycle cryogenic cooler which maintains the laser operating temperature down to 10°K. Laser temperature is maintained and stabilized by a control feedback circuit which also provides an additional frequency tuning mechanism (in addition to current tuning) for better mode selection. The utilization of this cooler instead of the liquid helium dewar was a major factor in the development of this practical, fieldable system. The laser radiation is collimated by an off-axis mirror,

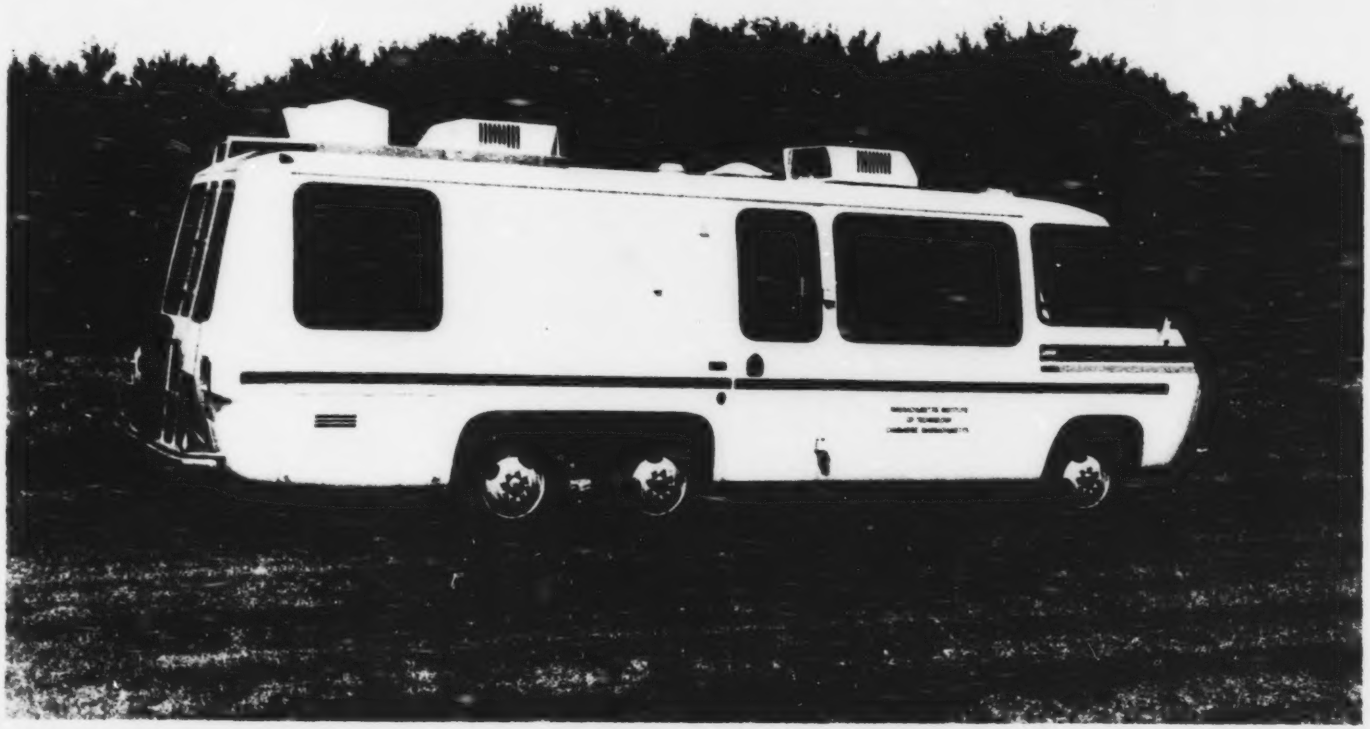


Fig.2. Diode laser monitoring van.

M-1, and transmitted to a remote corner-cube retroreflector. The returned beam follows the incident path back toward M-1 which refocuses it onto an InSb infrared detector situated behind a 10-cm calibration cell. In order to minimize the effects of atmospheric turbulence on system sensitivity, a derivative spectroscopic technique is employed in which the laser is frequency-modulated at 10 kHz at the pollutant gas absorption line of interest.

Calibrations of the long-path measurement are performed with calibration cells containing known concentrations of $CO\text{-}N_2$ mixtures at atmospheric pressure. Several mixtures are used to establish the system response curve (i.e., signal vs. CO concentration). This procedure can be applied both on top of the long-path CO burden; or for "in-house" short path (i.e., no long-path CO contribution) by placing a secondary retroreflector in front of M-1. Therefore, an effective "zero" concentration reading for the system is obtained when an empty calibration cell is used in the "in-house" short-path configuration.

This laser monitoring system was incorporated into the mobile van shown in Fig. 2. The van is 26 ft. long and weighs approximately 10,500 lbs with equipment. The inside view of the van is shown in Fig. 3 where some parts of the system are visible, such as the optical table, calibration gas bottles, electronics panel, and the closed-cycle cooler. The table is supported directly on the ground (rather than on the floor of the van) for optical stability. The vertical column on the table is of a similar design to that of a periscope for directing the beam through the roof onto the remote retroreflector.[7] Infrared alignment is aided by a telescope system. 300° directional coverage of the transmitted beam is provided by rotating the periscope column.

The laser monitoring system can and has operated around-the-clock, unattended in the 1975 RAPS study, except for the calibration checks mentioned above, and liquid N_2 refill of the InSb detector (every 10 hours).

In Section 2 of this report, the results and accomplishments of the 1975 RAPS study are summarized. Monitoring data and discussion are presented in Section 3. System accuracy and error analysis are described in Section 4.

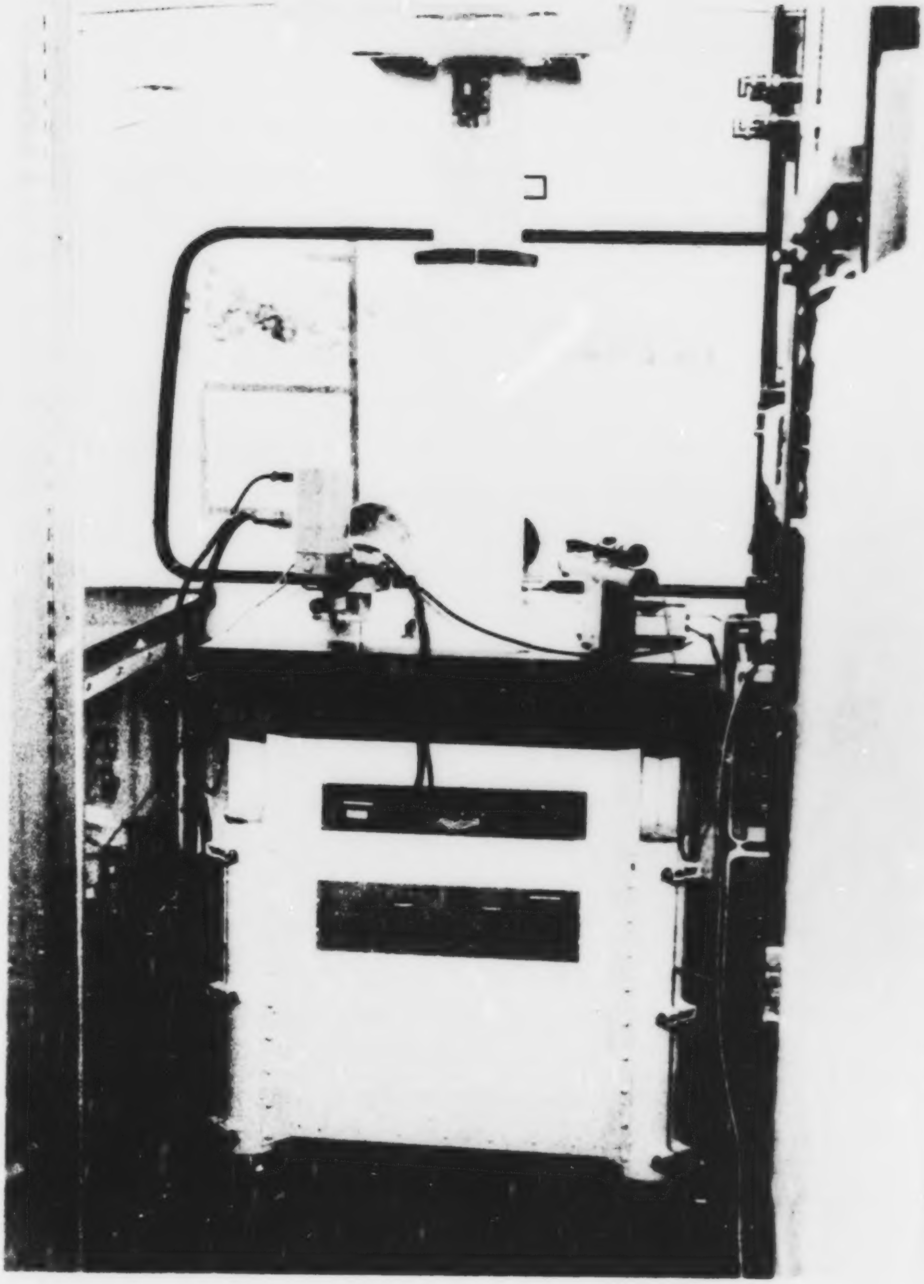


Fig.3. Inside view of monitoring van.

Conclusions and recommendations for future work are presented in Section 5. Finally, Appendix A includes all the data obtained during the 1975 study plotted on a standard 24-hour graph. For comparison purpose, the 1974 RAPS results are also shown in a similar manner in Appendix B. Appendix C is a reprint of a 1975 journal article which describes in detail the diode laser technique for long-path monitoring.

2. SUMMARY OF RAPS-1975 MEASUREMENTS

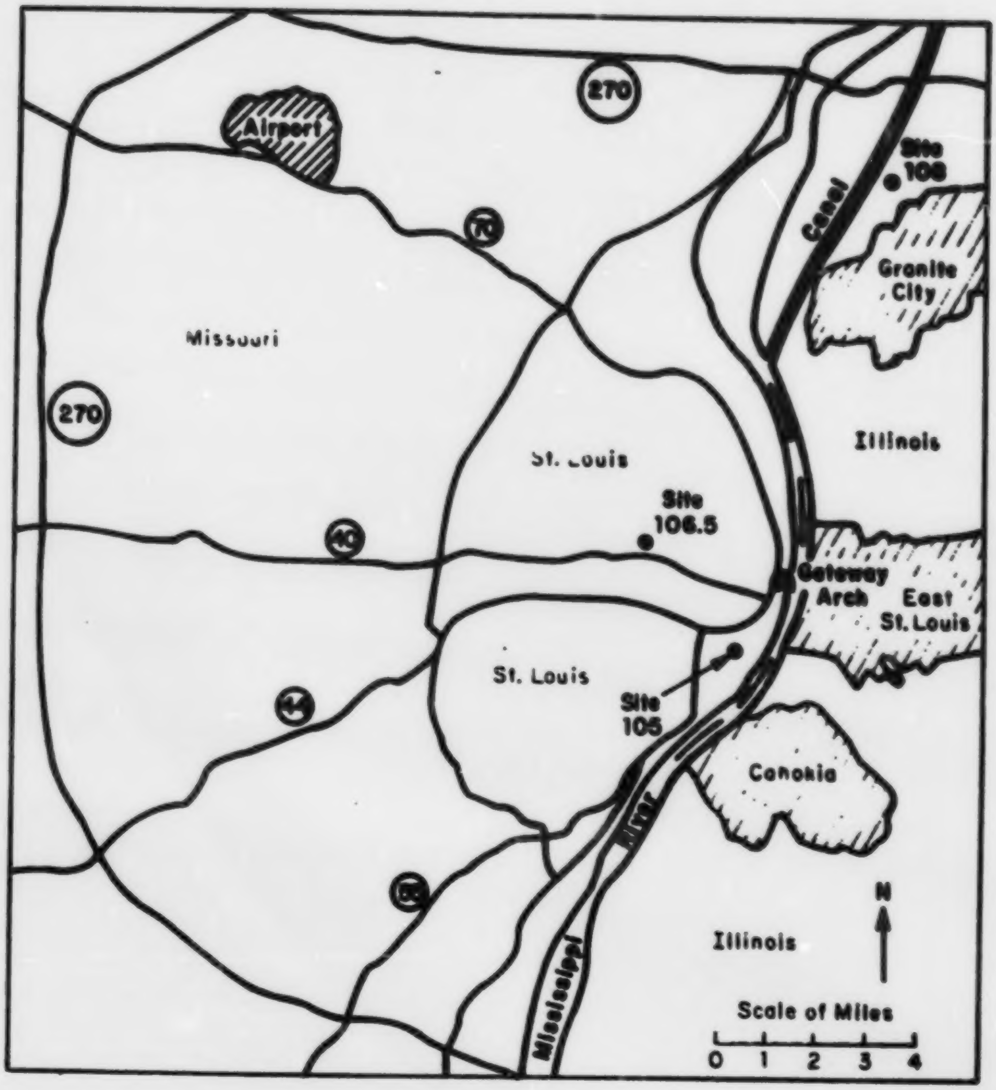
Long-path monitoring of ambient CO was conducted at two RAMS (Regional Air Monitoring Station) sites, 108 and 105, during the RAPS study from July to October 1975. The relative locations of these two sites are shown in Fig. 4. RAMS 108 is located on a farm north of Granite City, Illinois, and is considered to be a typical rural site. RAMS 105 is located in the downtown area of St. Louis, Missouri, and represents an inner city site where local industries and automobile traffic are important factors in the ambient pollution level.

The following accomplishments were made during the RAPS-75 measurement program:

1) Laser monitoring of atmospheric carbon monoxide (CO) over long ambient paths was performed at both sites for a total of over 40 days, including several weekends. In addition, around-the-clock monitoring was performed much of the time, made possible this year by the use of a new, longer-hold-time, liquid N_2-cooled detector in conjunction with the continuously operating closed-cycle cryogenic cooler for the diode laser.

2) The raw data have been analyzed and calibration error bars assigned. They have been digitized and plotted on a standard 24-hour form (see Appendix A), ready to be used by the EPA modelers.

3) In accordance with the Program plans, the semiconductor diode lasers used in RAPS-75 were purchased commercially. These measurements represent the first field application of diode lasers that were not fabricated at Lincoln Laboratory.


270
Airport
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Missouri
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St. Louis
Site 106.5
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Gateway Arch
East St. Louis
St. Louis
Site 105
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Canal
Site 108
Granite City
Illinois
Cahokia
River
Mississippi
Illinois
N
Scale of Miles
0 1 2 3 4

Fig.4. Area map of St. Louis, Missouri, showing locations of RAMS field sites.

4) Comparisons were made between the long-path CO results and the RAMS station point readings and/or data from a gas filter correlation instrument (GFC) located in the monitoring van. Excellent agreement was obtained for the three instruments under conditions of low pollution variability. Meteorological factors such as wind direction and velocity have to be considered, as a general rule, since the comparison is between a path monitor (laser) yielding space-integrated CO data, and point measurements from the RAMS and GFC instruments.[8]

5) The PbSSe diode laser was tuned to the P(9) or P(10) fundamental absorption lines of CO at 2103 or 2107 cm^{-1}, respectively. At Site 105 an unknown atmospheric pollutant was found to have absorption lines near these particular CO lines, which sometimes interfered with off-line-center measurements during periods of high CO concentration and long path lengths (> 1 km). This interference problem was minimized by reducing the path length (to 0.26 km), which permitted the monitoring of high concentrations without detuning the laser. On the basis of measurements performed subsequently in the Laboratory, the interfering pollutant appears to be an industrial effluent, since tests of raw automobile exhaust in this frequency range did not show any interfering gases. Further tests will be needed to identify this pollutant. Compared to interference-free CO monitoring with lasers operating on the P(4) line at 2126.69 cm^{-1} during RAPS-74, the frequency region of 2103 - 2107 cm^{-1} is definitely inferior for monitoring and should not be used unless absolutely necessary.

6. During long-path monitoring, particularly at Site 105, the laser frequency was often found to drift from its optimum value over a period of several hours, causing a change in calibration. An automatic frequency control (AFC) circuit was developed to "lock" the laser frequency onto the CO absorption line being monitored. With this AFC circuit, calibration was found to remain stable to within ± 2% over a 25-hour period of continuous monitoring.

7. A second diode laser operating at 5.3 μm for monitoring nitric oxide (NO) was mounted next to the "CO" laser inside the cooler, and long-path

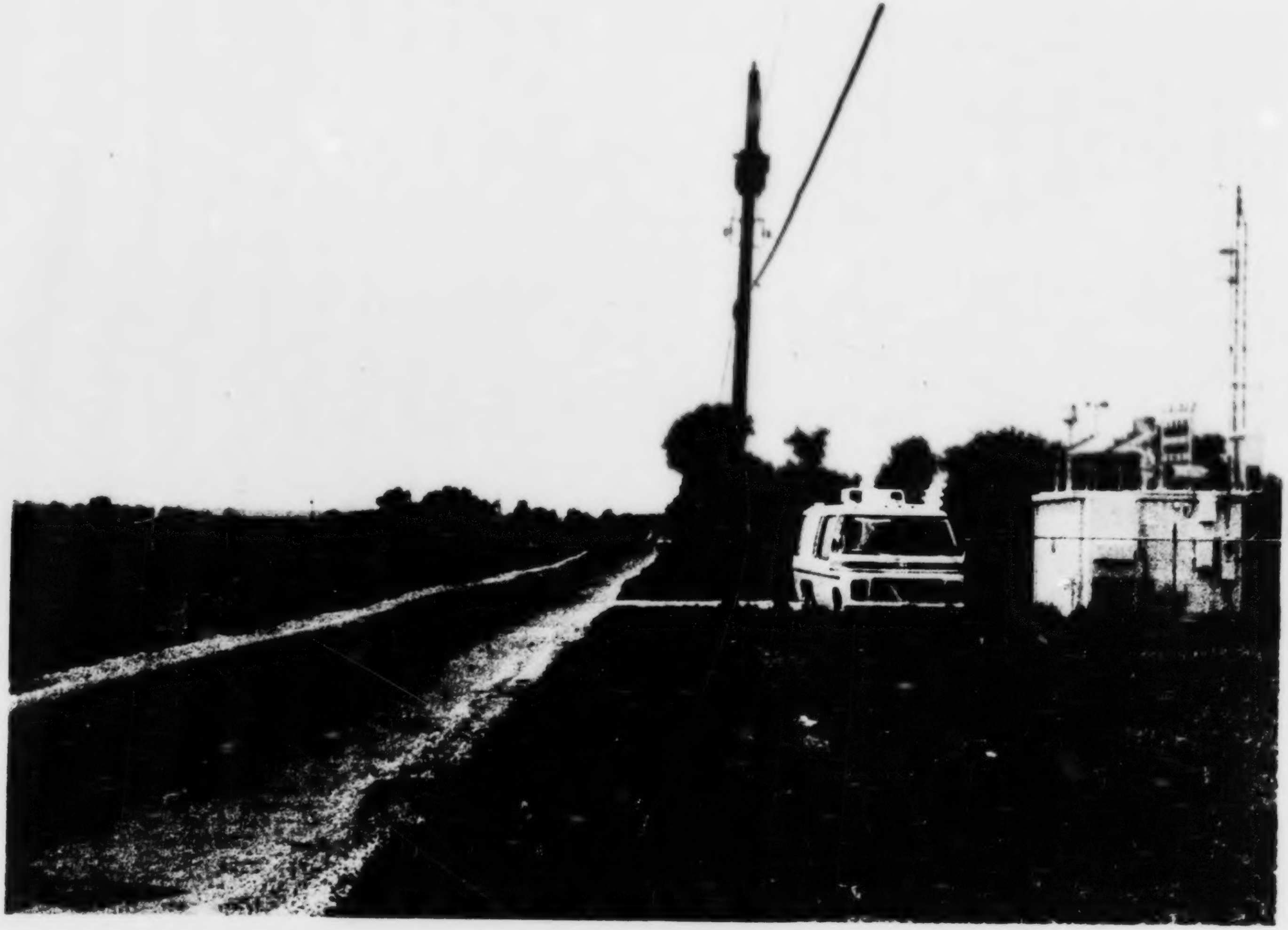

Fig.5. Photograph of RAMS Site 108, where long-path CO monitoring was performed from 7 July to 4 August 1975.

transmission of either beam was demonstrated by simple, repeatable optical adjustments of the off-axis mirror and beam-splitter.

8) EPA personnel were involved very closely in RAPS-75 measurements, and good progress has been made in the transfer of technology of the long-path diode laser system.

3. RAPS-75 MEASUREMENTS DATA

A. RAMS Site 108, Granite City, Illinois, 7 July - 4 August 1975

During the period from 7 July to 4 August, the laser monitoring van was located next to the RAMS station on this rural site, as shown in Fig. 5. Because of its remote location, the CO concentration here is usually low and relatively uniform; but with winds from the SW quadrant, pollution from the St. Louis metropolitan area becomes a factor; and from the southerly direction, pollution from vehicular traffic and industries in Granite City is expected to become important.

Figure 6 shows a typical 24-hour monitoring period at Site 108. The ambient CO concentration is plotted as a function of hour-of-day in Central Standard Time. The path length to the retroreflector was 0.34 km in the northerly direction. The continuous trace is the long-path laser result replotted with a 30-second time constant from the original data. The circles and crosses represent, respectively, the validated hourly averages of CO concentrations at the site from the GFC instrument and the RAMS station gas chromatograph. Fairly good agreement is obtained between these three measurements on this particular day of low CO level. The agreement between a path monitor and point readings usually indicates a fairly uniform and static pollution concentration.[8] This condition probably developed due to a favorable wind direction (not directly from St. Louis or Granite City) of ESE-SE, as indicated in Fig. 6. Calibrations of the laser monitor are indicated by the letter "C" at the appropriate times. For this 24-hour period, a 10% calibration fluctuation is noted, and the zero drift (in ppm) is also indicated. The combination of these two parameters largely determines the error range

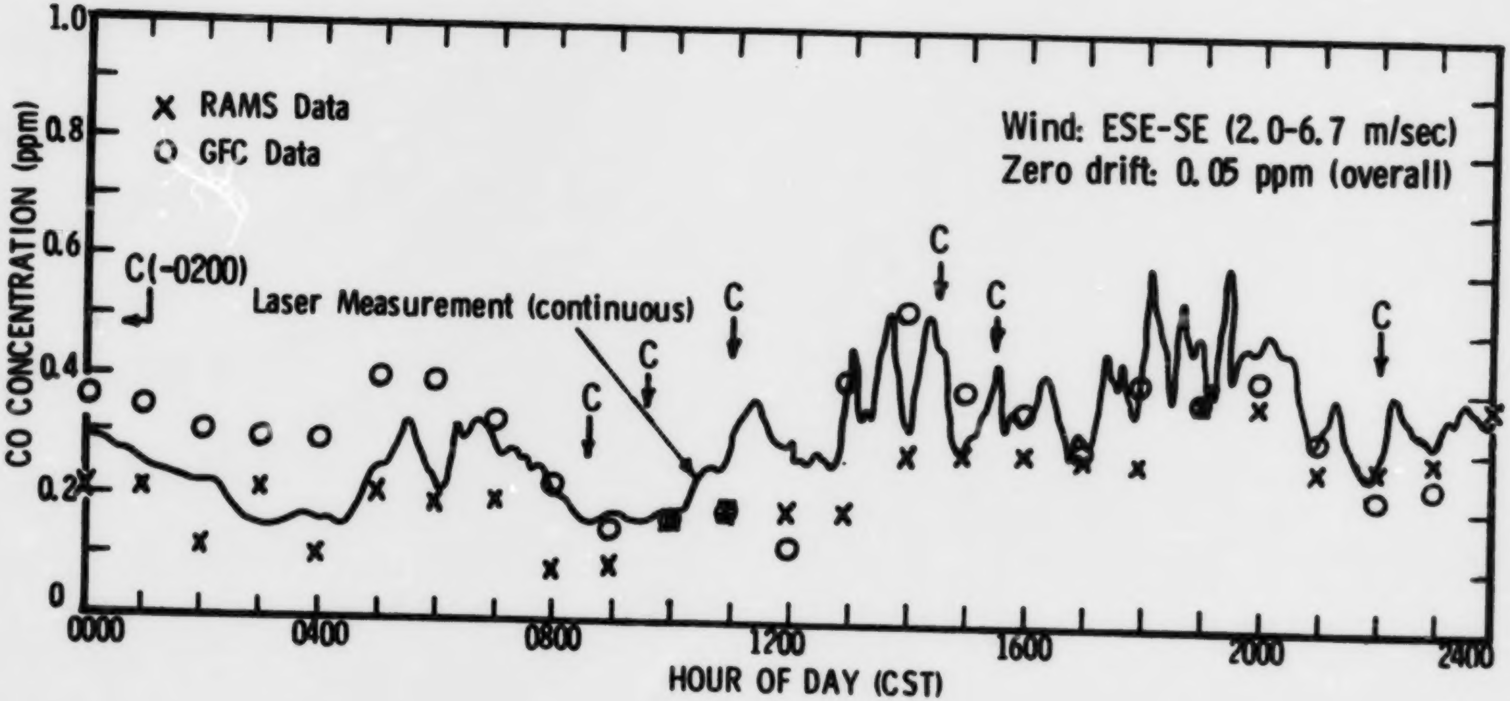

Fig.6. Around-the-clock CO monitoring on 1 August 1975 at RAMS 108. Distance to retro = 0.34 km. Monitor direction: north.

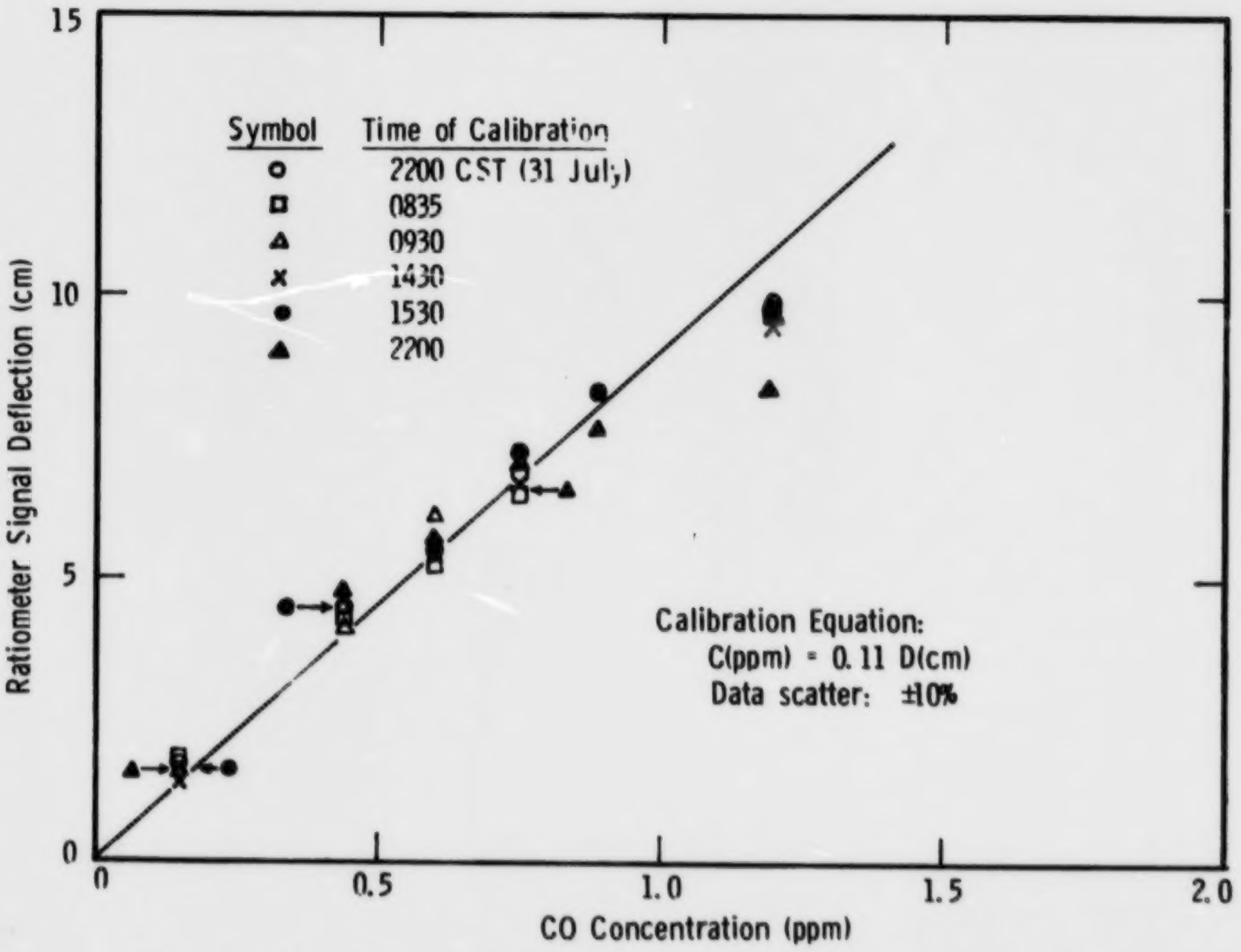

Fig.7. CO calibration curve for long-path laser monitoring on 1 August 1975 at RAMS 108. Distance to retro = 0.34 km.

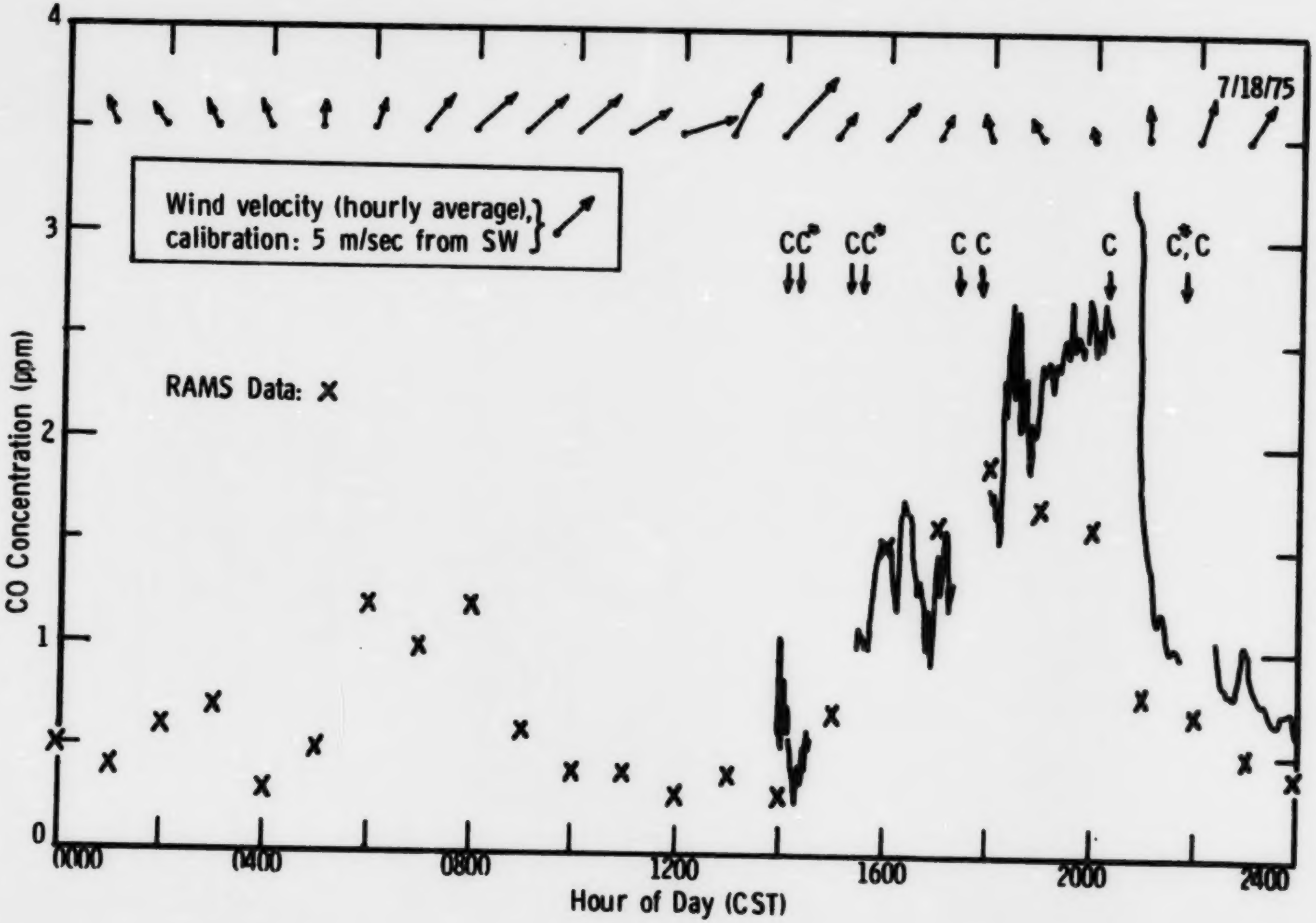

Fig.8. Long-path CO monitoring at RAMS 108 on 18 July 1975. Distance to retro = 0.2 km. Monitor direction: north.

of the CO results. In this case, an uncertainty of ± 10% in the laser monitored CO data is assigned.

The laser system calibration curve for the above results is shown in Fig. 7. The signal deflection on the strip chart recorder is plotted on the y-axis as a function of various effective CO concentrations over the long path (in ppm). For example, a 6.75-cm deflection was obtained for 5000 ppm CO in the 10-cm calibration cell, equivalent to 0.74 ppm over the 0.68-km total path. During this period no definite drift trend was observed for the set of calibration points performed at various times; therefore, these points can be fitted by a visual or least squares technique into the following calibration equation for data analysis:

$$C(\text{ppm}) = 0.11\ D(\text{cm}). \tag{1}$$

An uncertainty value of ± 10% was obtained on the basis of scatter of the calibration points about the above equation. If the calibration curve shows a definite drift toward higher or lower slope over a period of time (due to laser frequency drift), then a time-dependent calibration equation is used for data analysis during that period of time.

Figure 8 illustrates a different type of pollution data, recorded at Site 108 on 18 July 1975. The CO concentration was found to peak at around 1800 to 2000 hours on the basis of both the long-path and the RAMS data. The wind direction and speed are also plotted in order to determine any correlation. Further analyses of this type are still being worked on. The letter "C" designated the usual "in-house" calibrations and "C*" the "ambient-calibrations", obtained by inserting the appropriate concentrations of calibration gases in the 10-cm cell into the returned beam path to superimpose corresponding signals on top of the ambient level deflection.

Figure 9 shows the CO results obtained by the laser monitor and RAMS station on 23 July 1975. The path length and monitor direction to the retroreflector were changed from 0.34 km north to 0.75 km west at 1600 CST. The objective of this type of change was to observe any correlative variation between the long-path and RAMS readings due to wind direction or other relevant meteorological parameters.

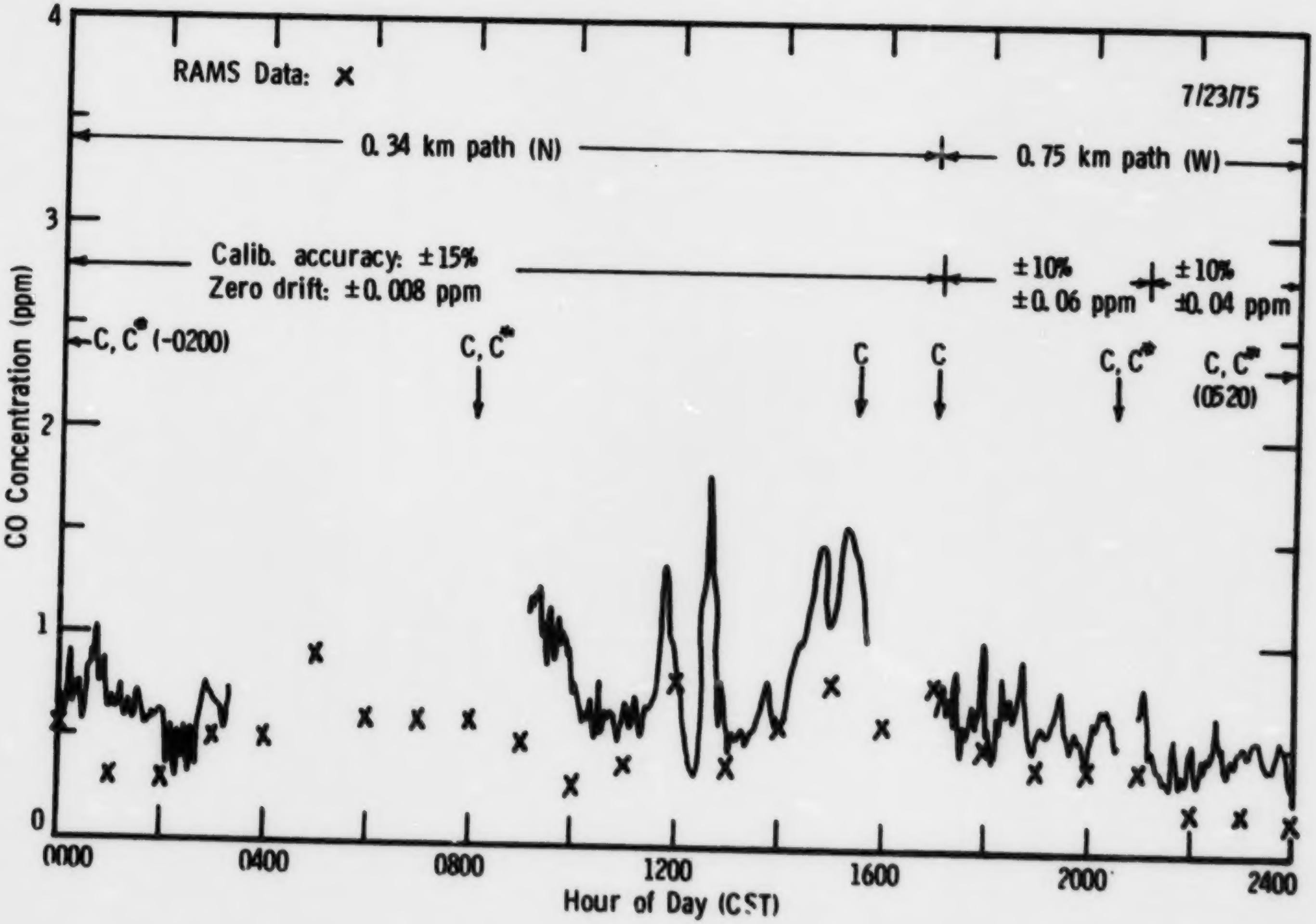

Fig.9. Long-path CO monitoring at RAMS 108 on 23 July 1975. Distances to retro = 0.34 and 0.75 km. Monitoring directions: north and west.

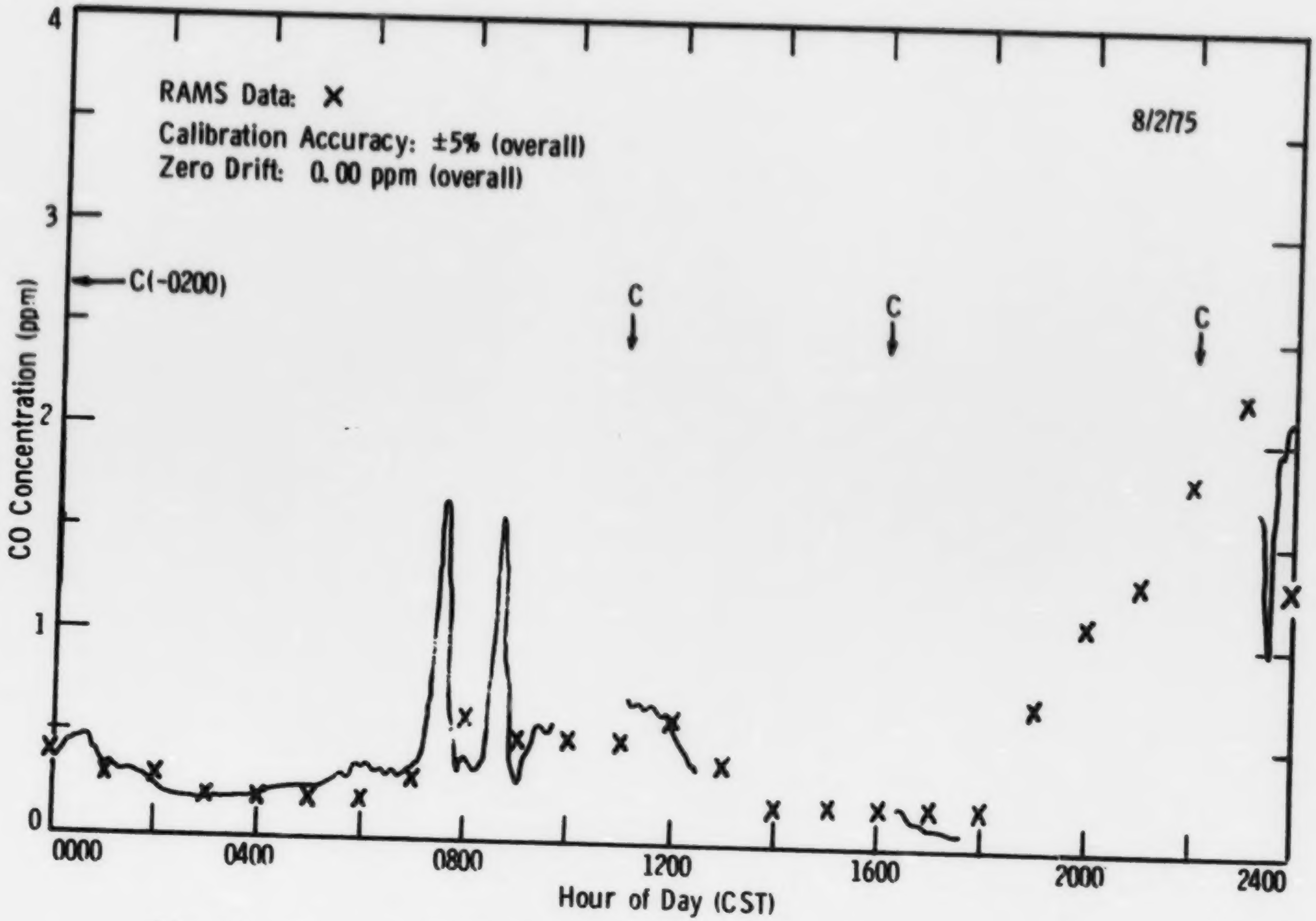

Fig.10. Long-path CO monitoring at RAMS 108 on 2 August 1975. Distance to retro = 0.34 km. Monitoring direction: north.

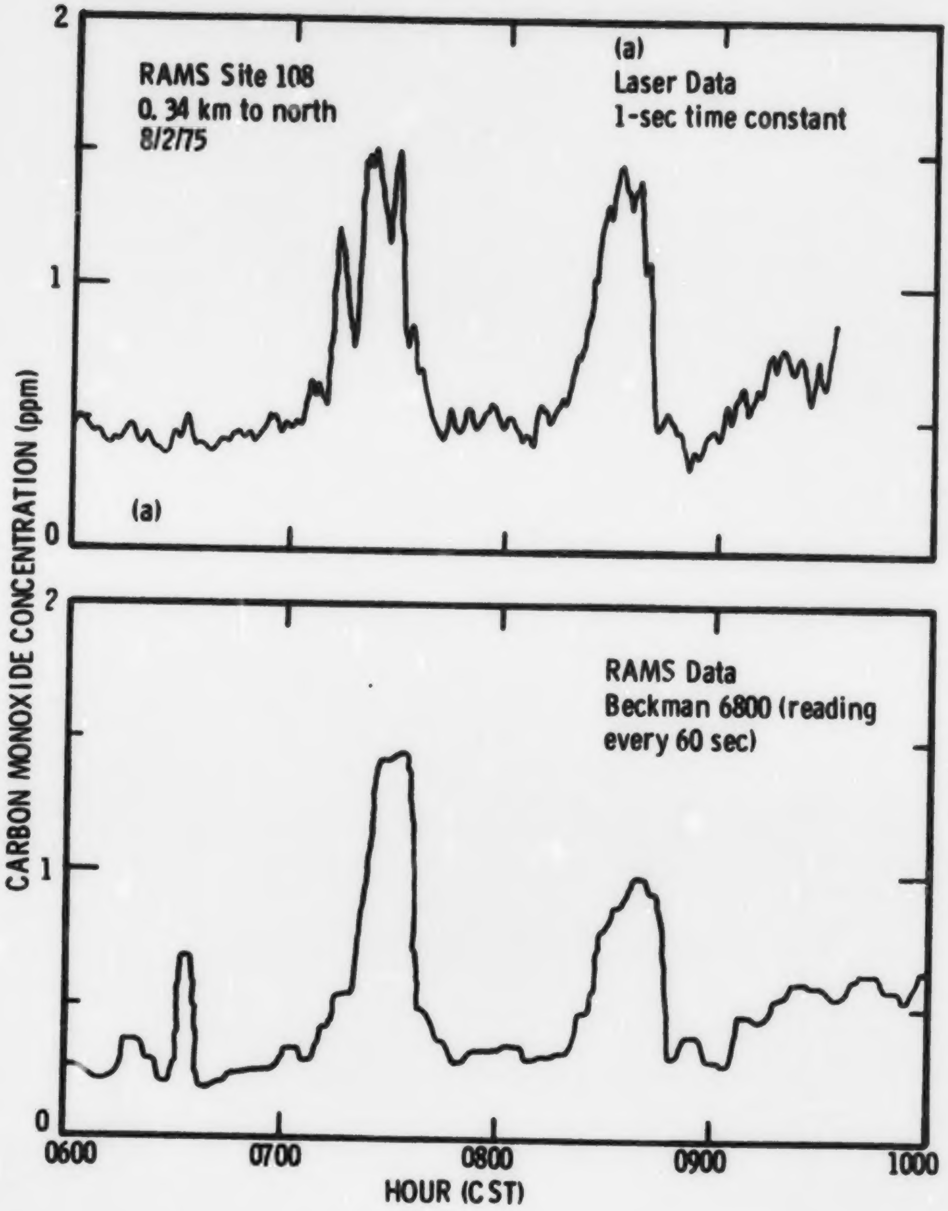

Fig.11. Comparison of CO monitoring results, from 0600 to 1000 CST on 2 August 1975 at RAMS 108, between (a) the long-path laser monitor and (b) RAMS' Beckman 6800 gas chromatograph. Time constant is 1 sec for (a), and 1 min. for (b).

Figure 10 illustrates interesting results from CO monitoring on 2 August 1975. Two sharp peaks were recorded by the laser monitor around 0800 CST. Due to their fast rise and fall times, correlations with the RAMS hourly readings at 0800 and 0900 CST are poor. However, excellent correlation is obtained using minute-by-minute averages of RAMS and 1-second time constant laser data for this dynamic period between 0600 and 1000 CST, as shown in Fig. 11.

A total of 21 days of long-path CO data is plotted on the standard 24-hour graph and included in Appendix A. These results should be useful for pollutant model development, in conjunction with site meteorological data from the RAMS station.

B. Site 105, Downtown St. Louis, Missouri, 6 August - 10 September

Ambient CO concentrations were monitored on Site 105 from 6 August to 10 September. This site is located between buildings of the Monsanto Chemical Co. (0.6 km away) and Anheuser Busch Brewing Co. (1 km away). The retroreflectors were stationed on top of each building in order to change directions and path lengths. For example, Fig. 12 shows the laser monitor path to the top of the Monsanto Building. A much more dynamic behavior of the ambient CO level is expected for this geographic location compared to RAMS 108.

Figure 13 shows typical results of CO monitoring, over a 0.65-km path (1.3 km total path), between 0000 and 0800 hours CST. In the afternoon the laser beam direction was changed by 180° and the path length was reduced to 0.13 km. Correlations between the laser result and RAMS data seem to be better for the shorter path and lower concentration in the afternoon (1600 - 2400 hours). This is the expected behavior for the comparison between a point sampling instrument and a path-integrated system, particularly in an area with many local emission sources.[8]

Figure 14 shows an interesting CO level comparison between a week day and a Sunday over the same path of 0.12 km in the southerly direction. The ambient CO level on Friday, 22 August, is shown in Fig. 14(a), in which a peak concentration of over 5 ppm between 0800 and 1000 CST occurred. In

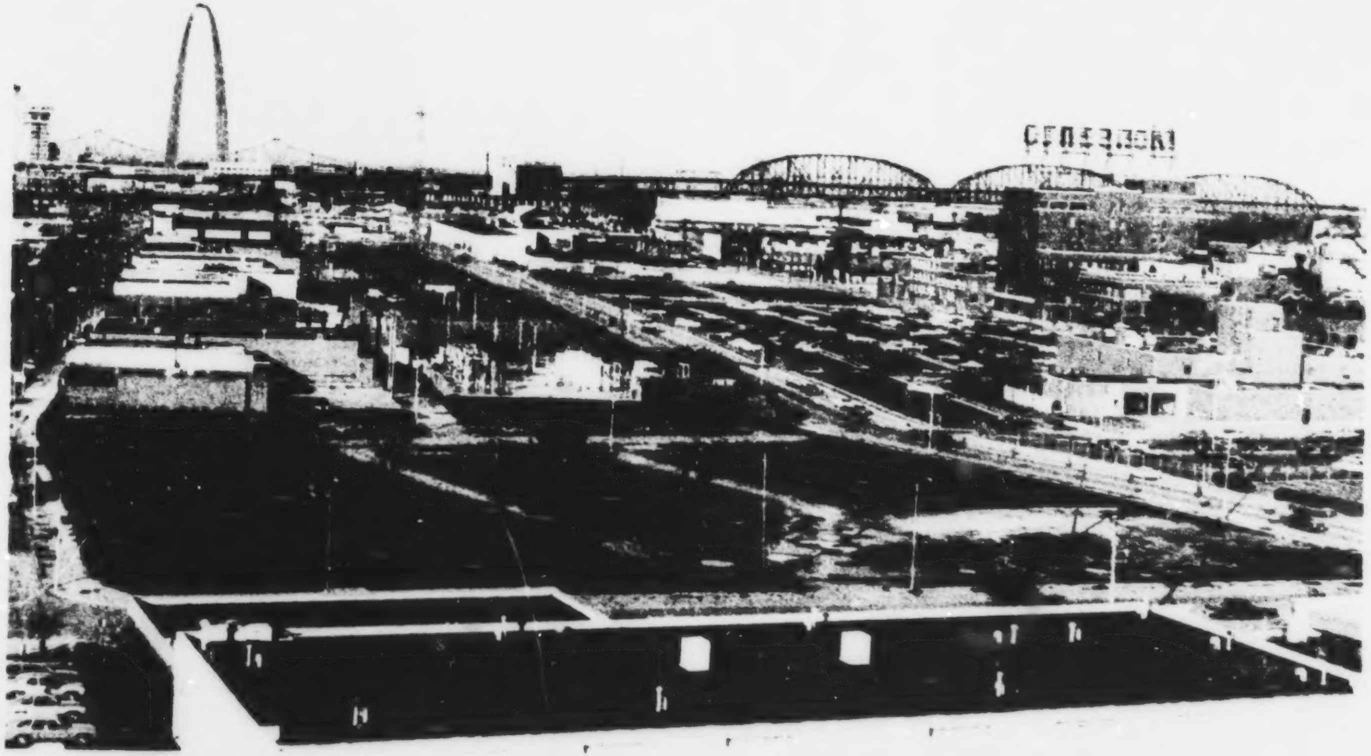

Fig.12. Photograph taken at RAMS Site 105 in downtown St. Louis from van twoard top of Monsanto Building. Distance = 0.62 km (one of the laser monitoring paths).

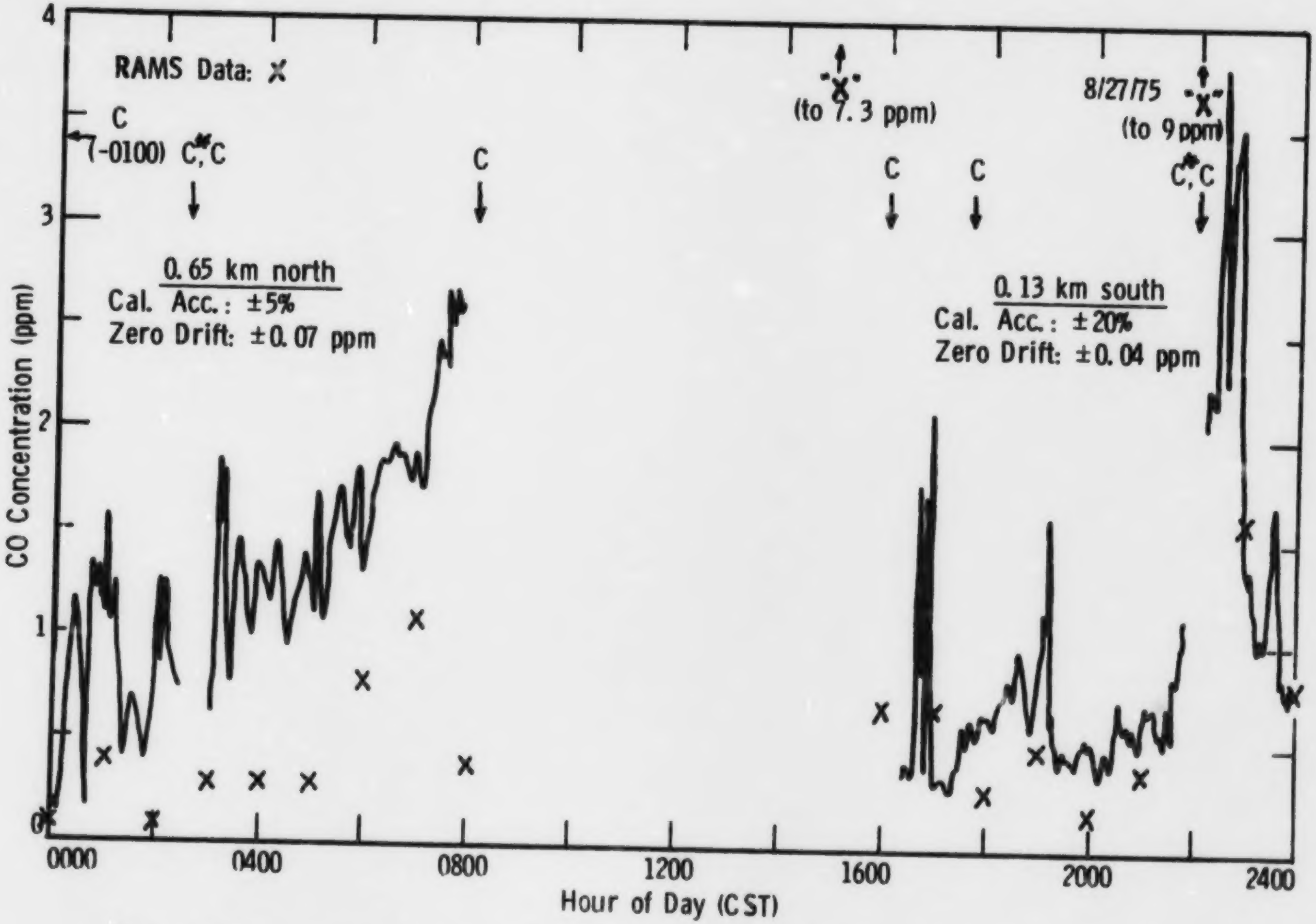

Fig.13. Long-path CO monitoring at RAMS 105 on 27 August 1975. Distances to retro = 0.65 and 0.13 km, in northerly and southerly directions, respectively.

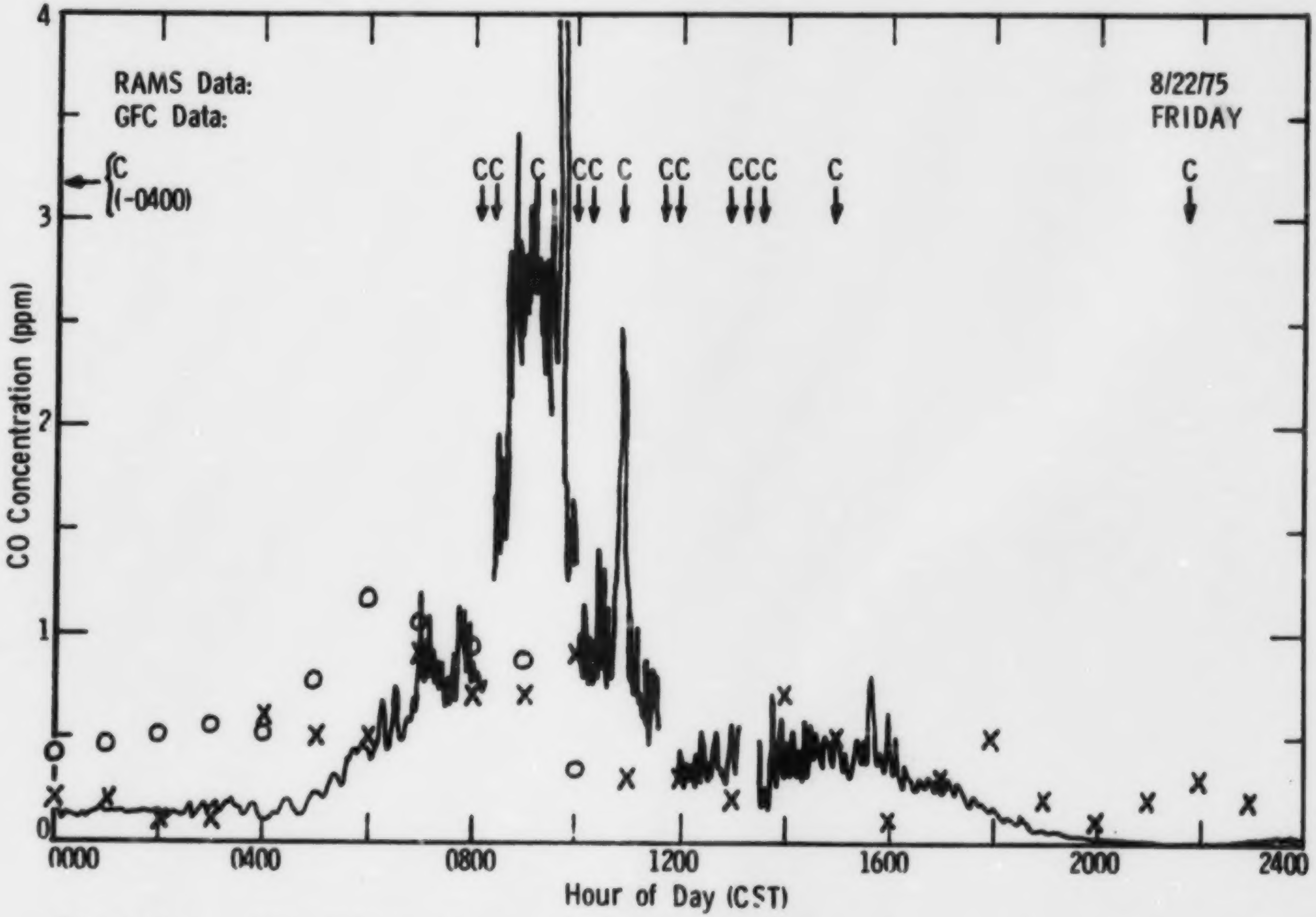

Fig.14(a). Comparison of CO concentration measured over identical paths (0.12 km southerly) on 22 August 1975 (Friday) at RAMS 105.

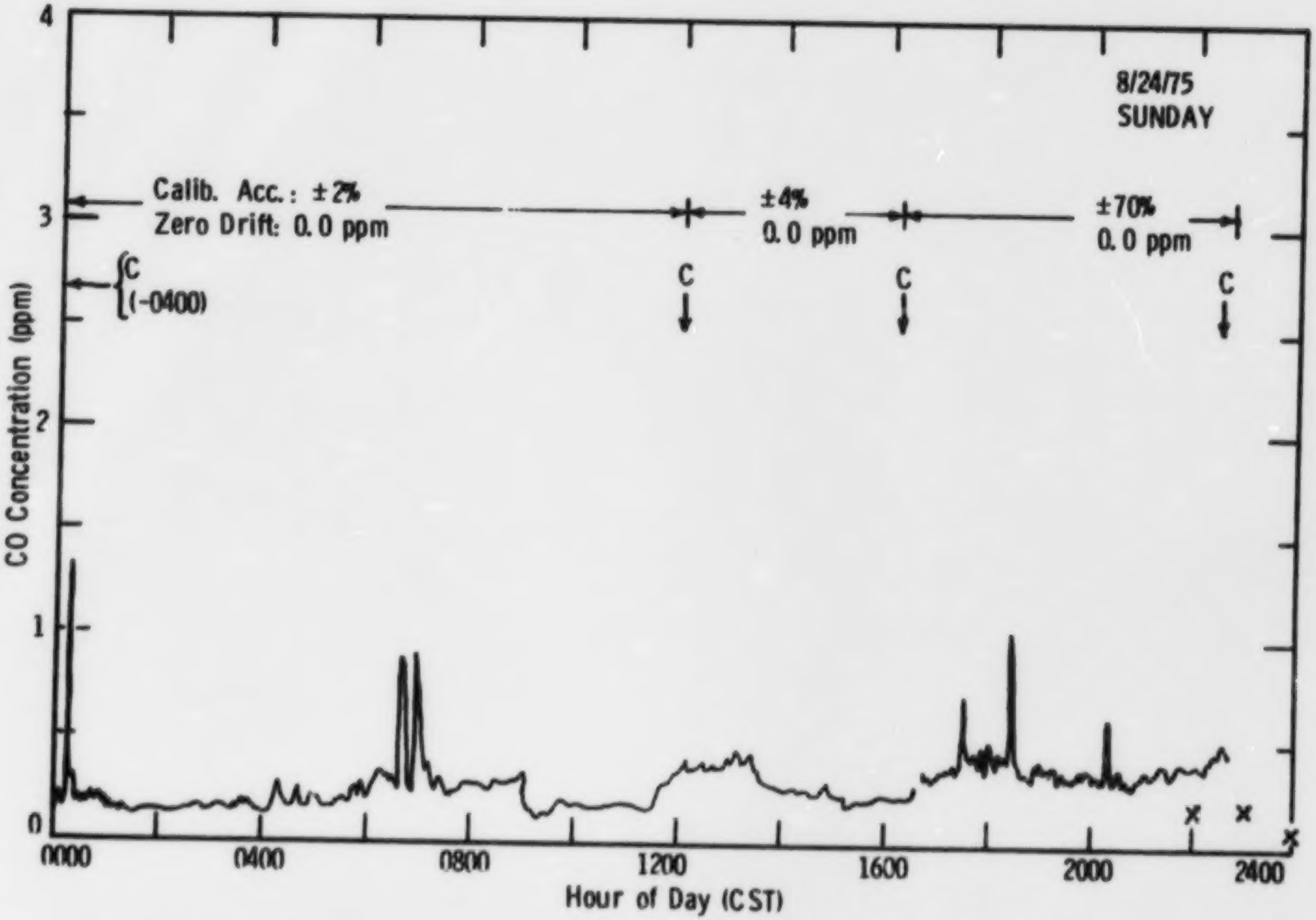

Fig.14(b). Comparison of CO concentration measured over identical paths (0.12 km southerly) on 24 August 1975 (Sunday) at RAMS 105.

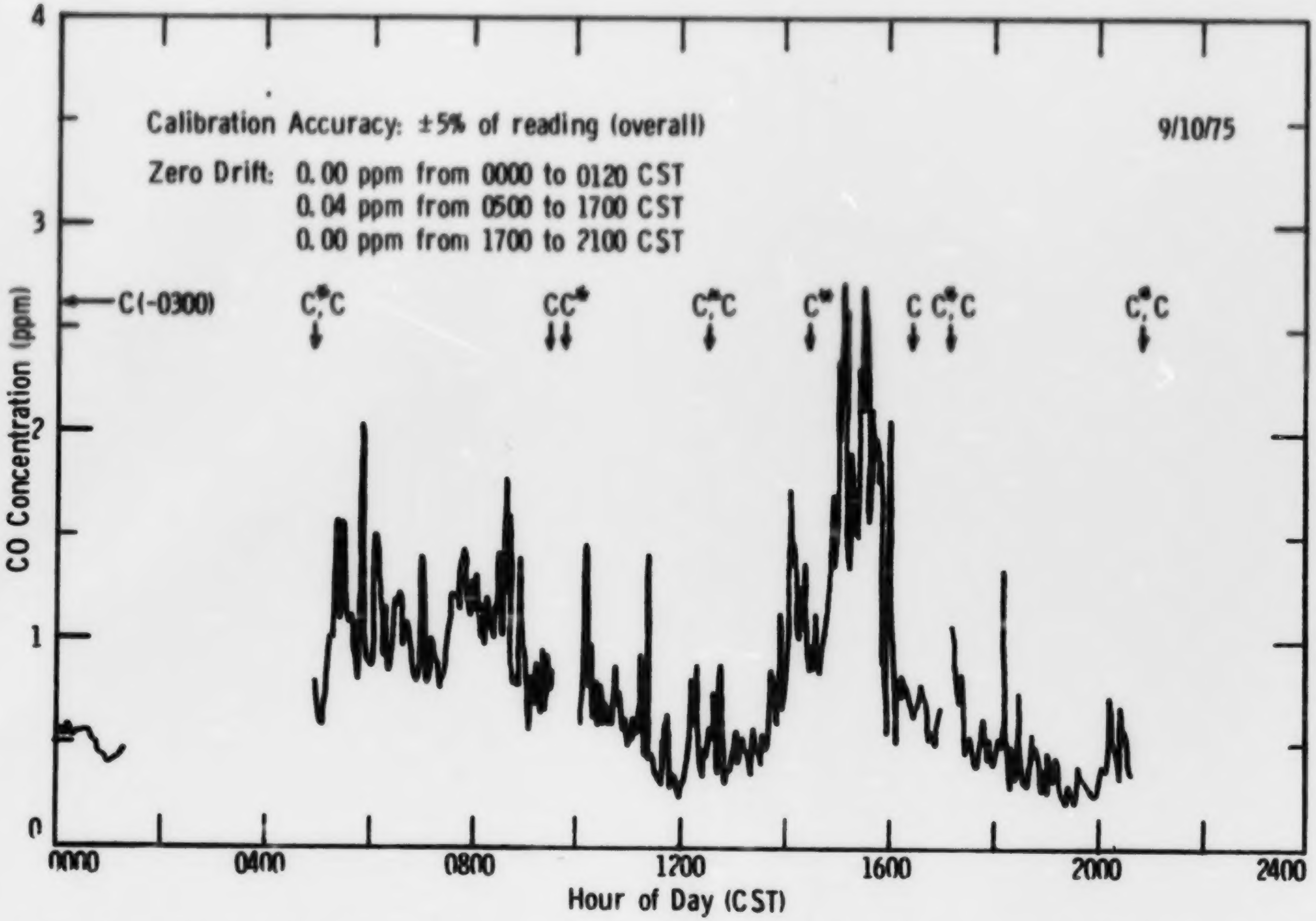

Fig.15. Long-path CO monitoring at RAMS 105 on 10 September 1975, with AFC circuit installed. Distance to retro = 0.13 km. Monitoring direction: south.

addition, wide fluctuations in the CO level were measured during business hours, between 0700 and 1600 CST, compared to quiet periods of 0000 - 0700 and 1600 - 2400 CST; even though the same 30-second plotting time constant was used throughout the 24-hour period. Figure 14(b) shows the CO concentration over the same path on Sunday, 24 August. Except for a few spikes, the result is very similar to the measurements at Site 108 during periods of low pollution. The level of CO over the monitored path on this Sunday was generally below 0.5 ppm. The large uncertainty in the data between 1600 and 2300 CST is due to calibration drift during this period.

A change in calibration with time was usually found to be caused by a steady drift in the laser frequency, and brought about the need to calibrate every hour or so. In order to reduce the number of such calibrations, an Automatic Frequency Control (AFC) circuit was used to stabilize the diode laser frequency. Details of the AFC circuit will be described in the next section. With the incorporation of this feedback control circuit, calibration drift on the order of 2% was observed over a 25-hour period. Figure 15 shows results of long-path laser monitoring on 10 September 1975, after installation of the AFC circuit. A 5% calibration accuracy was achieved over the entire monitoring period.

The results of 20 days of monitoring at Site 105 are included in Appendix A of this report.

At this site, an unexpected pollutant was found to have spectral absorption lines in the neighborhood of the CO lines we used for monitoring. The absorption line of the interfering species was located between the CO P(9) line at 2107 cm^{-1}, and the CO P(10) line at 2103 cm^{-1}. The unknown species probably came from one of the industries around Site 105, since it was not in evidence at the rural Site 108 in Illinois. In addition, recent laboratory tests showed that automobile exhaust contains no such interference. During the monitoring period, whenever this interference occurred, we reduced the path length to 100 - 200 meters in order to permit laser operation at line center, and thus minimize this effect. A new diode laser chemically tailored to the interference-free region of 2127 - 2133 cm^{-1} will have to be used in the future to completely eliminate this interference problem.

4. SYSTEM ACCURACY AND DATA ERROR ANALYSIS

The usefulness of any monitoring system is determined by its accuracy under various conditions. In this year's RAPS program, a great deal of time was spent verifying the calibration and checking zero drift and other quality assurance factors. An error bar for each data run was determined by noting the calibration variation and zero drift, and considering other laser system operation factors such as percentage of returned laser power and laser amplitude and frequency stability. Most of the data have error bars from ± 10 to ± 15%; however, a few monitoring periods have as high as ±75% uncertainty.

The following is a list of possible sources of error in the diode laser monitoring system:

1. Amplitude fluctuation of the diode laser emission.

2. Frequency stability and drift of the laser emission.

3. Scattering and turbulence effects on the transmitted laser intensity.

4. Effect of ambient temperature on the CO absorption line.

5. Difference between self-broadening and N_2 broadening of the CO absorption line, and its effect on calibration.

6. Calibration drift and nonlinearity, difference between the "in-house" and "ambient" calibrations due to multiple spatial modes of the diode laser.

7. Interference by other atmospheric pollutants.

The major sources of error were found to come from items 2, 6, and 7 in the above list. A detailed discussion will be given for them after brief considerations of the less significant factors (items 1, 3, 4, 5).

1. *Laser Amplitude Fluctuation.* Less than a 1% power variation was detected in the laser emission prior to long-path transmission. This is usually insignificant compared to the amplitude variation due to atmospheric turbulence and scattering.[3,4]

3. *Scattering and Turbulence Effects.* The amount of laser power returned to the detector from long-path transmission is primarily determined by the amount of atmospheric turbulence and scattering. It was found that losses of incident laser power over the path of up to 75% can be tolerated using the automatic gain control amplifier in the Ithaco ratiometer system for analyzing the derivative/ratio signals.

4. *Ambient Temperature Effects on the CO Absorption Line.* If the outside temperature rose to 40°C (104°F) or dropped to 0°C (32°F), the calibration would be in error by only 1.8%, since the pollutant gas linewidth is approximately inversely proportional to the square root of the absolute temperature.

5. *Difference between Self-Broadening and N_2 Broadening of a CO Absorption Line.* Atmospheric absorption lines of CO over the long path are pressure-broadened by 760 torr of air (mainly N_2); however, the same line of an equivalent concentration in the 10-cm calibration cell is broadened by both N_2 and CO molecules. Since the *slope* of the line is used to monitor pollutant concentrations, the exact broadening mechanisms are important in calibrations. Fortunately, this effect is small in the CO case due to its having similar air- (or N_2) and self- (CO) broadening coefficients[9] (4.4 MHz/torr vs. 5.1 MHz/torr). For example, the highest CO concentration mixture bottle used for calibration was 30,000 ppm (equivalent to 3 ppm over a 1-km total path), and the calibration error due to self-broadening in this case is only 0.24%.

The *major* accuracy-determining factors -- laser frequency stability, calibration drift, and interference -- are considered below:

1. *Frequency Stability.* The derivative/ratio technique for monitoring requires the diode laser to operate at a particular frequency around the line center of a CO absorption line (usually at the inflection point for

maximum sensitivity). Calibrations using various CO concentrations are performed at that frequency. The laser frequency was often found to drift about the preset point over a period of a few hours, thus causing calibrations to vary with time. This effect was found to be much more noticeable during normal working hours of 8:00 a.m. to 5:00 p.m., particularly at Site 105. The heavy use of air conditioners in buildings and offices in the area caused the line voltage in the van to fluctuate; and this may have affected the cooler operation and laser temperature. The laser frequency was, as a result, slightly temperature-tuned, resulting in a different calibration. Normally, a time-dependent calibration curve was used for data analysis in this case.

To avoid the need for excessive calibrations under these conditions, an automatic frequency control (AFC) circuit must be used to "lock" the laser frequency onto the absorption line being monitored. An AFC circuit employing a second infrared detector and a second cell containing CO was used for this purpose during the early September measurements at Site 105. Any change in laser frequency was detected by the second detector, and the d.c. output from the phase-lock system was used to feed back to the laser a proper amount of control d.c. current (to ± 20 mA) to bring the laser back to its preset frequency.

This circuit operated successfully and calibration remained stable to within ± 2% over a 25-hour period of continuous monitoring.

2. Non-linear Calibrations and Different "In-house" and "Ambient" Calibrations. A non-linear calibration curve was sometimes found for higher concentrations of CO. This was the result of multi-frequency operation of the diode laser. Different "in-house" and "ambient" calibrations were also noted at times. This was due to different simultaneous spatial modes in the diode laser emission.

Ideally, a single-spatial mode, single-frequency laser is desired for long-path monitoring by differential absorption. More than one spatial mode can lead to differences between a short-path, in-house calibration and ambient calibration made over the long path (in which only one mode may be returning from the retroreflector). If both spatial modes have the same frequency characteristics, this problem is not as severe. Stripe-geometry lasers generally emit in a single-spatial mode, and such lasers were used during RAPS-74. The commercial lasers used in RAPS-75 were not of the stripe-geometry type, and more than one spatial mode was sometimes present. In order to correct for the effects of two or more spatial modes from the laser, calibrations were performed for both the in-house and ambient regimes, and the results compared. Where there was a significant difference, the long-path value was used to establish the calibration curve.

Non-linear calibration at the higher concentrations was also found when the diode laser was emitting multi-frequency modes. In this case, one mode might be frequency-mismatched and thus not absorbed by the CO line. To correct this effect, the data were fit with a quadratic calibration curve:

$$C\,(\text{ppm}) = \underline{a}D + \underline{b}D^2, \tag{2}$$

where C is the CO concentration in ppm, D the signal on the strip-chart recorder, and $\underline{a}$ and $\underline{b}$ empirical constants.

3. Interference by other Atmospheric Pollutants. At Site 105, an unexpected pollutant was found to have absorption lines in the neighborhood of the CO lines used for monitoring. An example of the interfering lines is shown in Fig. 16. In this figure, the y-axis corresponds to the recorder output of derivative/ratio signal (see Appendix C) as a function of laser current. Since the diode laser frequency is tuned by varying the current, the x-axis is then an effective frequency scale. CO P(9) (2107 cm^{-1}) line center is located at 591 mA. For maximum sensitivity, the laser current should be either 591.5 mA or 590.5 mA (at the inflection points of the line). Peaks from equivalent calibration mixtures of 1.2 and 0.4 ppm are shown, along with that of ambient level. Long-path derivative spectra of the absorption lines from the unknown atmospheric species were obtained at 588.7, 592.8, 596.6 and 600 mA. From this figure it appears that monitoring at

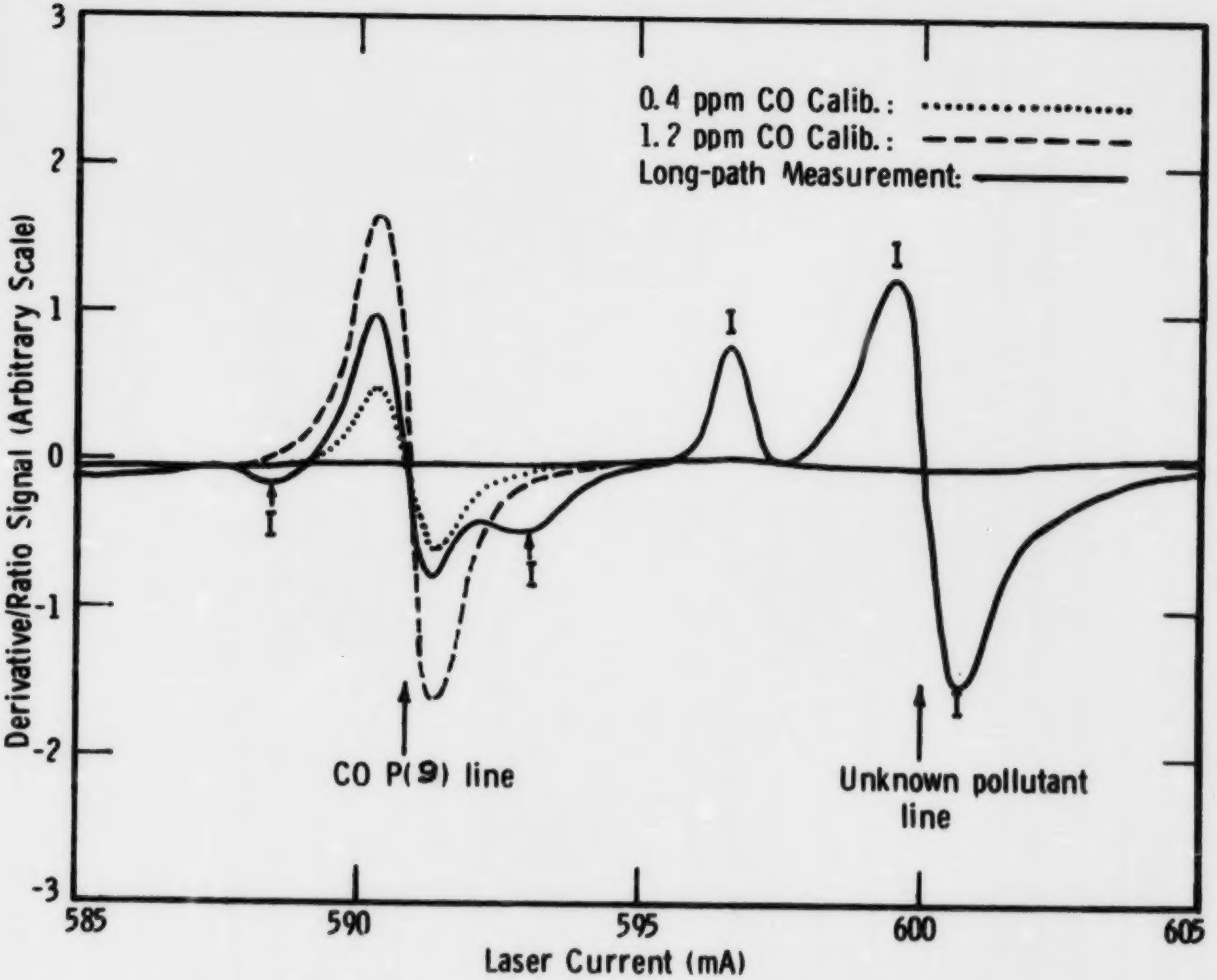

Fig.16. Derivative/ratio signal (proportional to CO concentration). Scans as a function of laser current (or frequency) through CO P(9) absorption line at 591 mA (2107 cm^{-1}), and absorption lines from unknown interfering pollutant at 588.7, 592.8, 596.6 and 600 mA.

591.5 mA or 590.5 mA can be performed with insignificant contribution from the interferences. However, for higher concentration or longer paths, close to 100% absorption can occur at these inflection points of the absorption line (i.e., not enough returned signal for monitoring). Under this circumstance we have to tune the laser further into the "wing" of the line; for example, at 615 mA or 630 mA, where interference does become a problem. The ideal solution to this problem is, of course, to use another diode laser that emits in an interference-free frequency region, such as the 2127 - 2130 cm^{-1} range utilized in the RAPS-74 program. Because both of the diode lasers available this year emitted radiation at around 2107 cm^{-1}, the field solution used was to reduce the path length so that monitoring at the peak signal at 617.5 mA became feasible again. Therefore, monitoring was performed during periods of high concentration, but at the expense of a shorter path length.

5. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE MONITORING

Successful CO monitoring over long paths was performed during the 1975 Regional Air Pollution Study (RAPS) of the U.S. Environmental Protection Agency. Over 40 days of monitoring were carried out at RAMS Sites 108 and 105. These data have been analyzed with assigned error bars, and are presented on 24-hour daily plots in Appendix A. Correlations with meteorological data are continuing in order to obtain relevant information for pollution modeling.

Some unexpected problems in calibration drift, non-linearity and interference were encountered this year; however, they were successfully minimized in the field. As these problems were caused, in part, by use of some of the first commercially-produced diode lasers, they are expected to diminish as more satisfactory manufacturing techniques are developed.

ACKNOWLEDGMENTS

We are pleased to acknowledge the assistance of J. O. Sample and J. V. Gormley in developing the laser monitoring system, and of the following personnel of the U.S. Environmental Protection Agency (or under contract with EPA) for their invaluable assistance during the Summer-75 period: L. W. Chaney, Michael Travis, Jeff Kochelek, Carol Chaney, George Russwurm, and W. A. McClenny. We also thank Dr. McClenny for his review of this report prior to final preparation.

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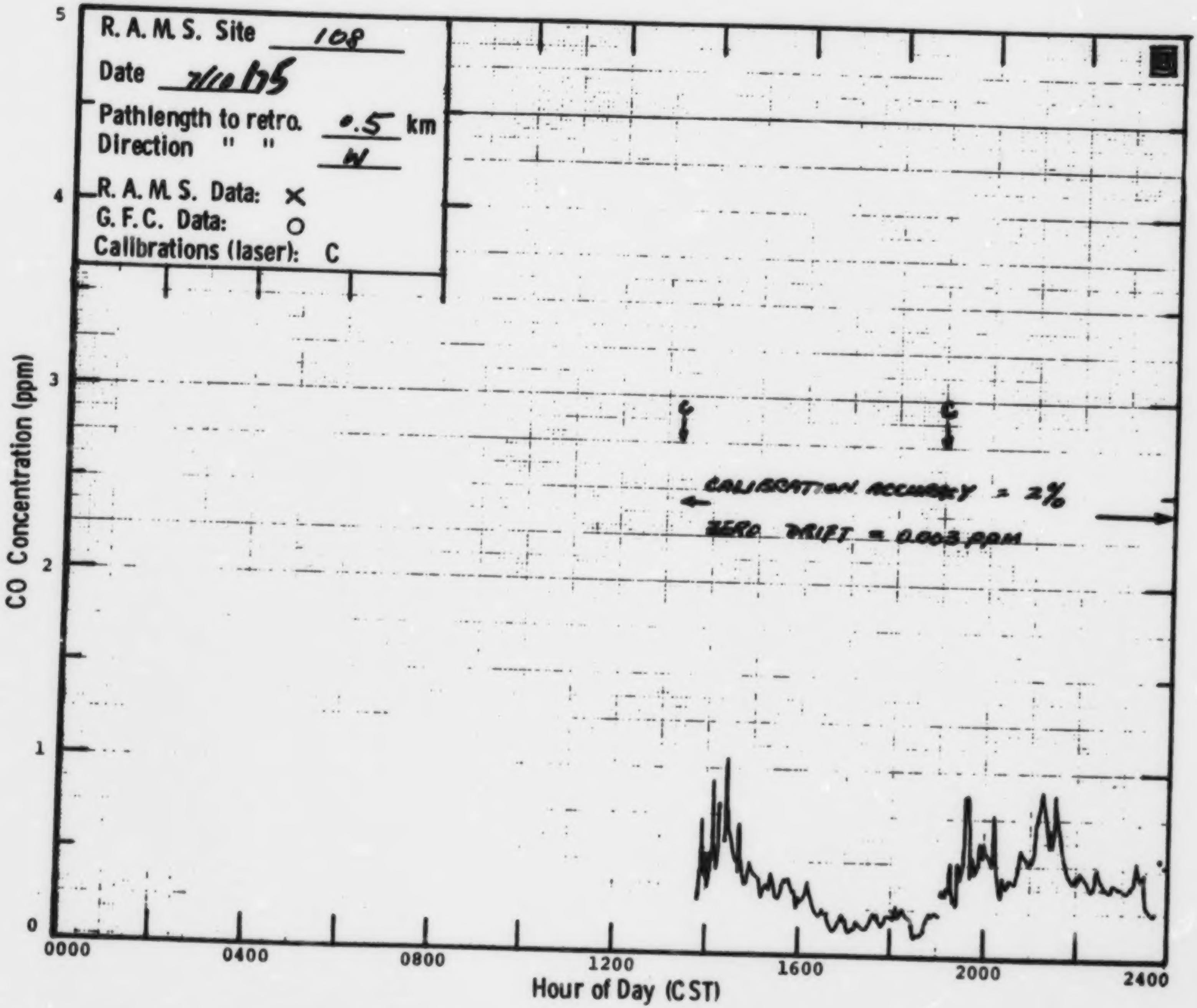
7. L. W. Chaney also contributed to the design of the periscope beam-directing system.

8. "Methodology for Comparison of Open-Path Monitors with Point Monitors," by W. A. McClenny, R. E. Baumgardner, Jr., Frederick W. Baity, Jr., and Rebecca A. Gray, Journal of the Air Pollution Control Association 24, 1044 (1974).

9. E. D. Hinkley and R. T. Ku, unpublished.

APPENDIX A

1975 RAPS Measurement Data



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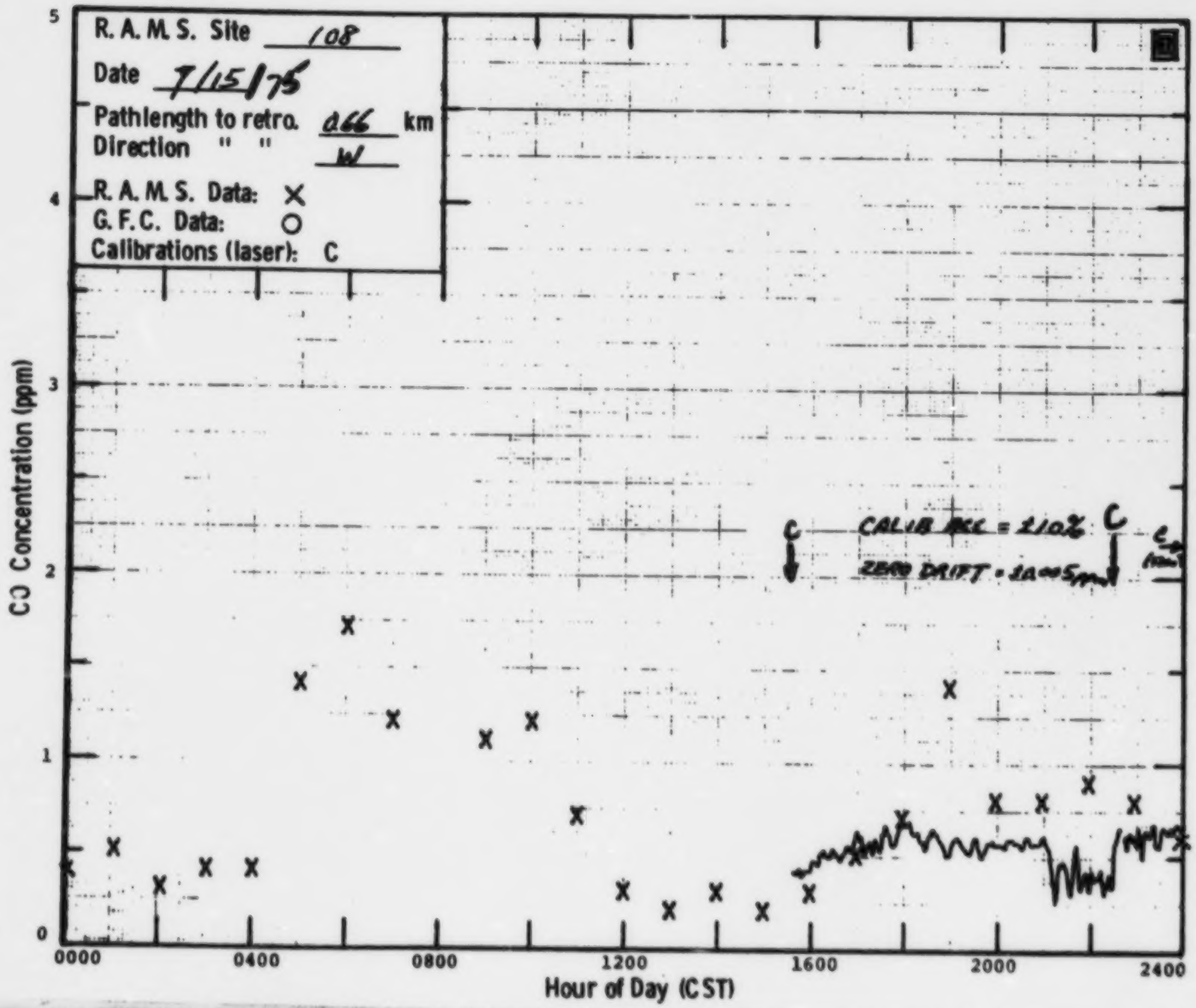
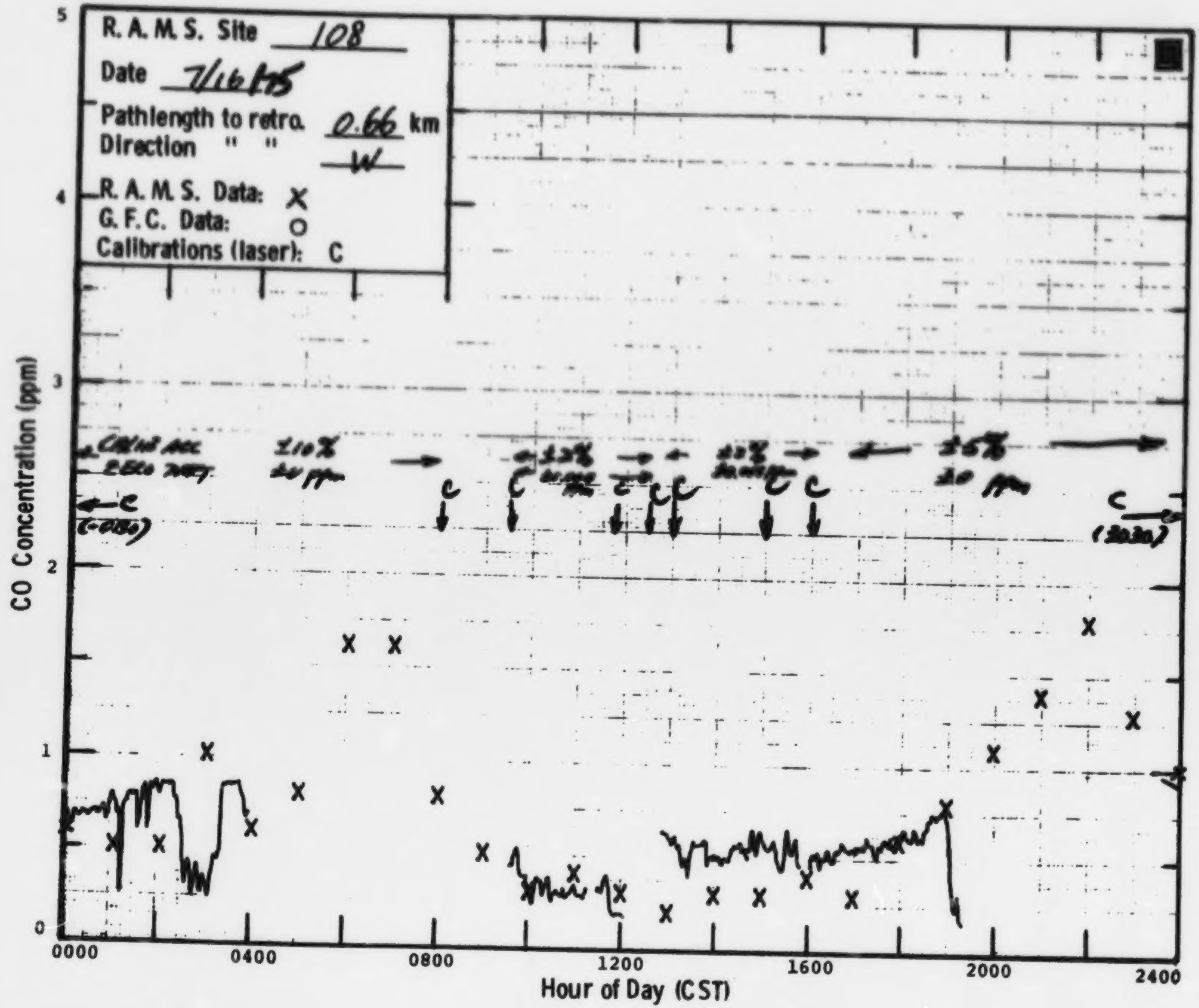
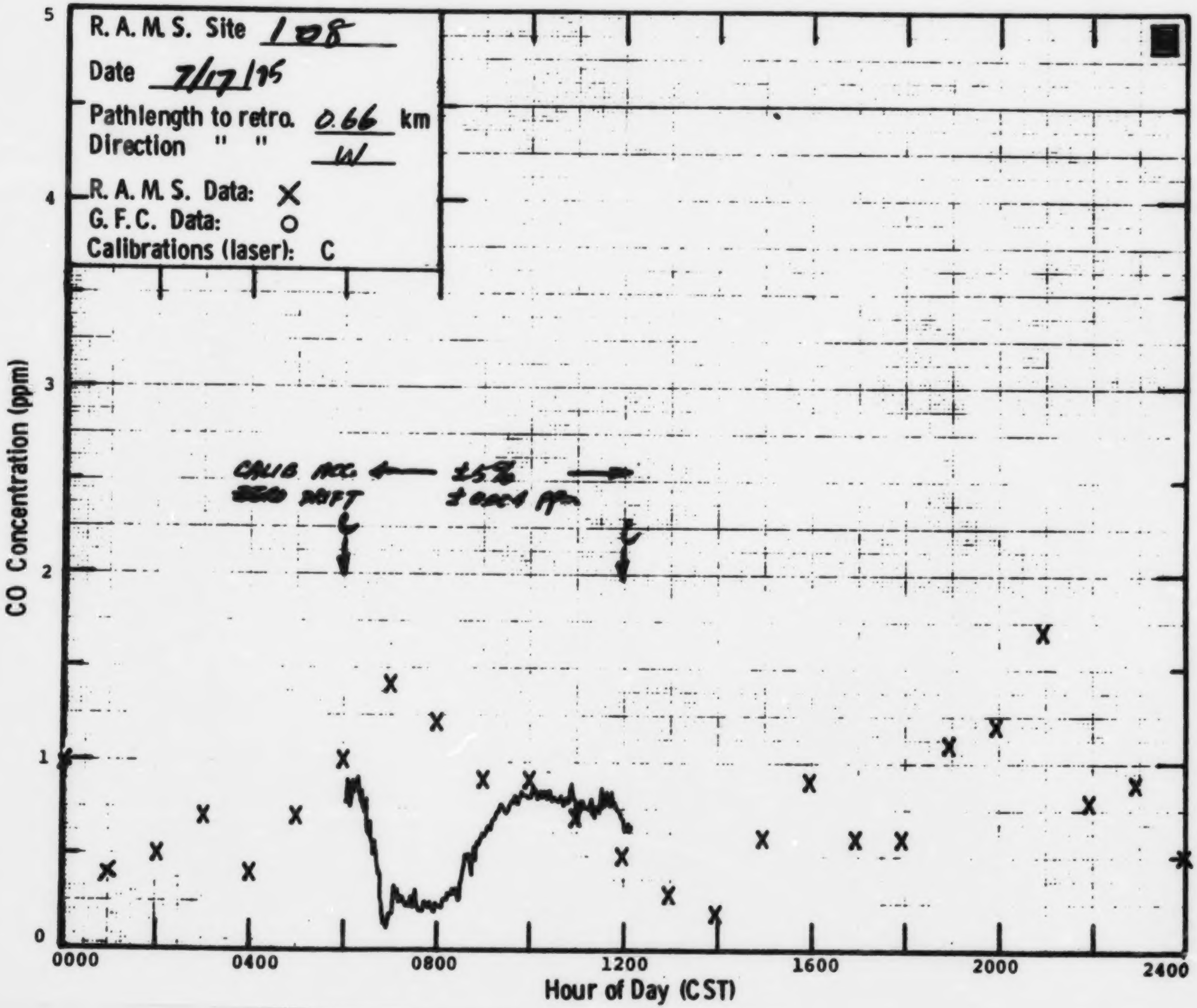
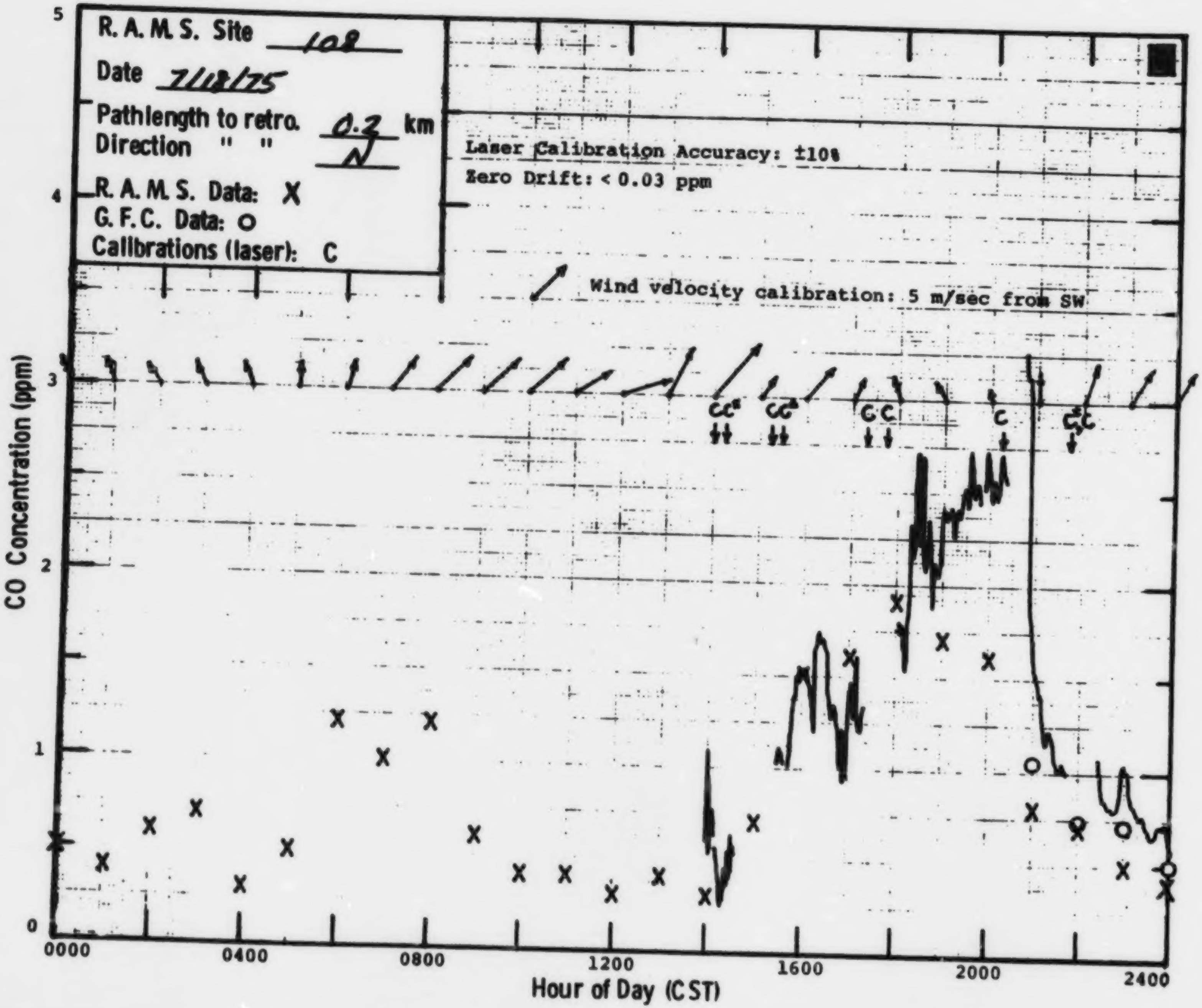
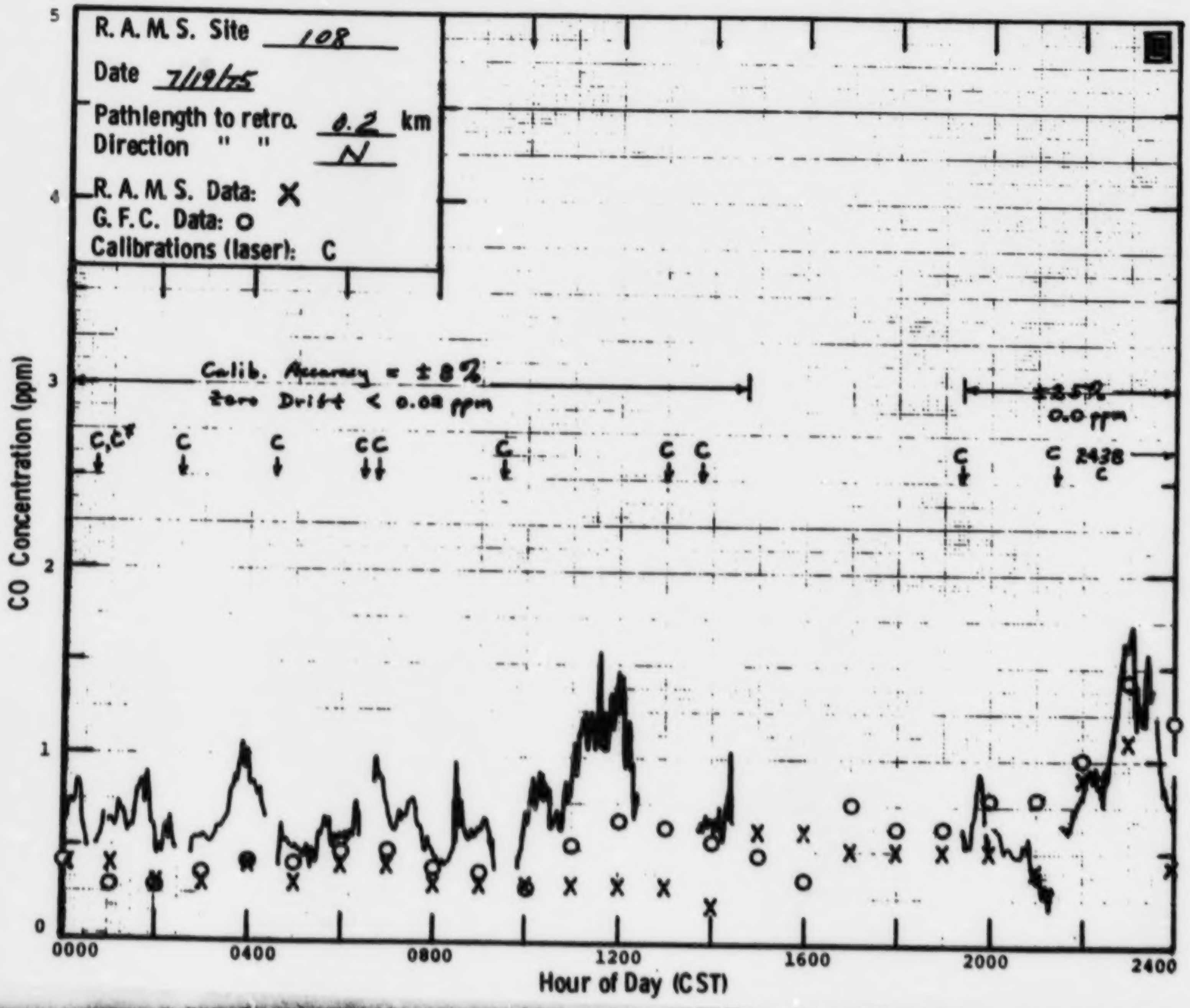
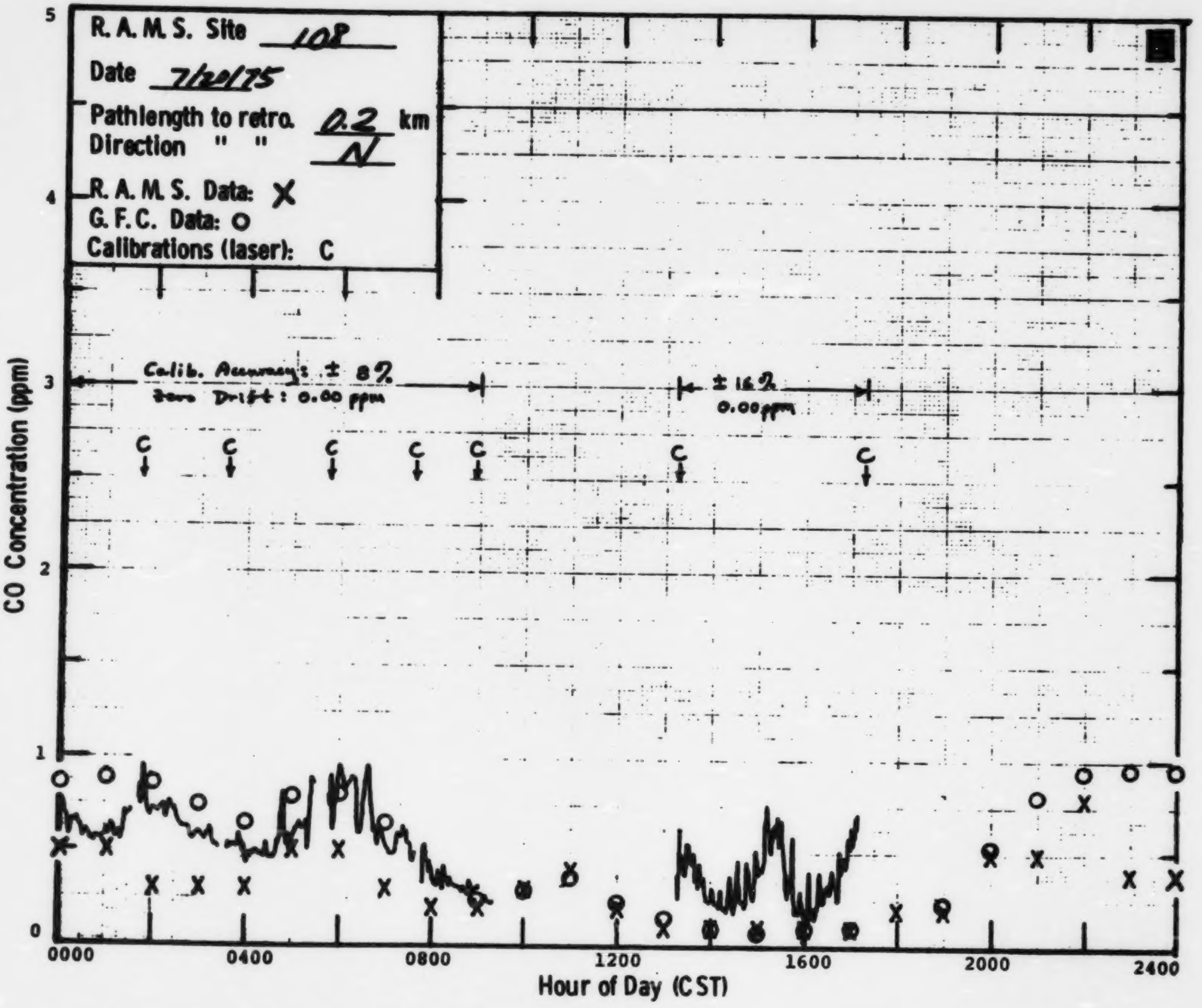

R. A. M. S. Site 108
Date 7/15/75
Pathlength to retro. .066 km
Direction " " W
R. A. M. S. Data: ×
G. F. C. Data: ○
Calibrations (laser): C
CALIB ACC = ±10%
ZERO DRIFT = ±.005 ppm
C
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)

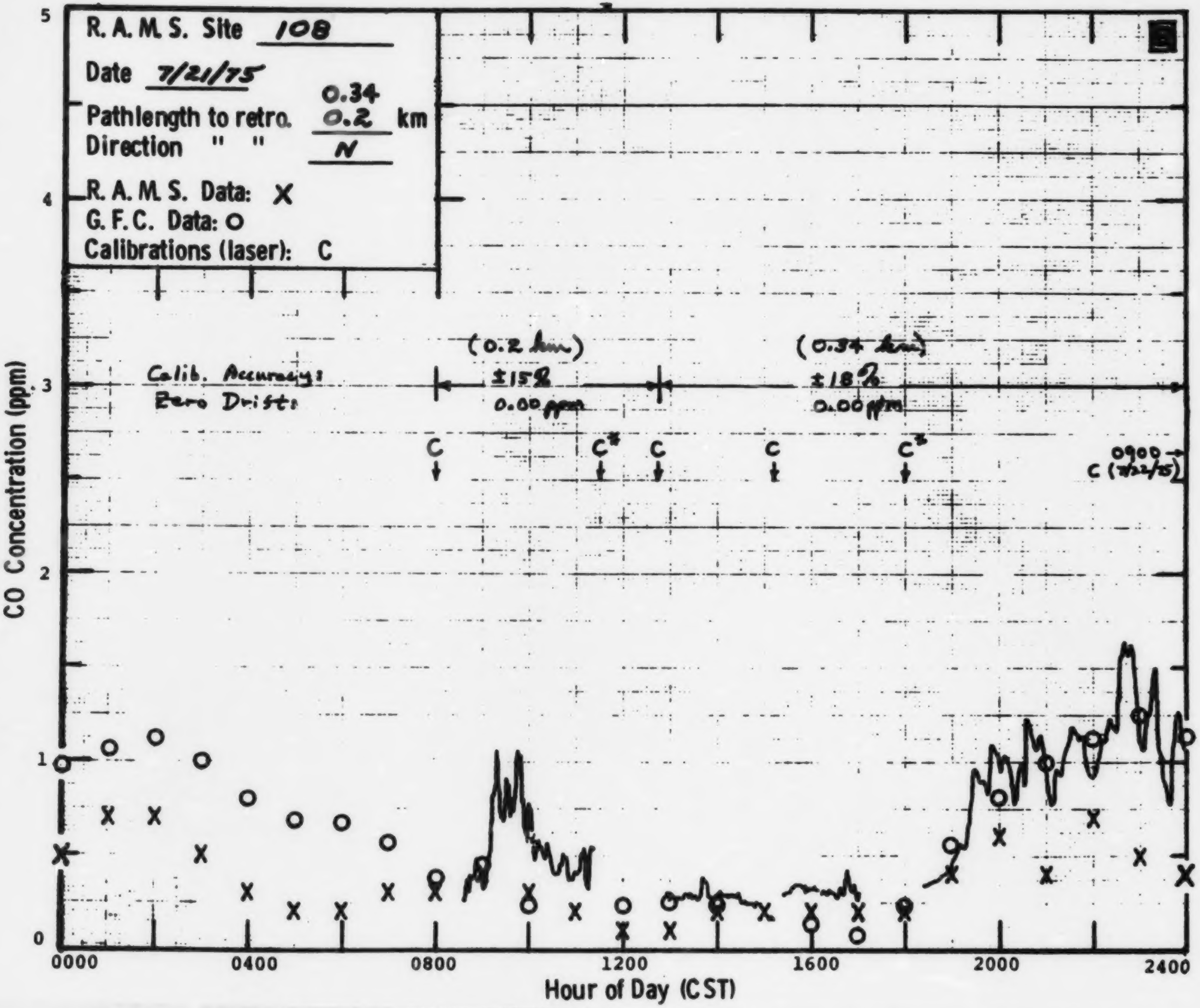

R. A. M. S. Site 108
Date 7/16/75
Pathlength to retro. 0.66 km
Direction " " W
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400
±10%
20 ppm
±5%
20 ppm
C
(2030)

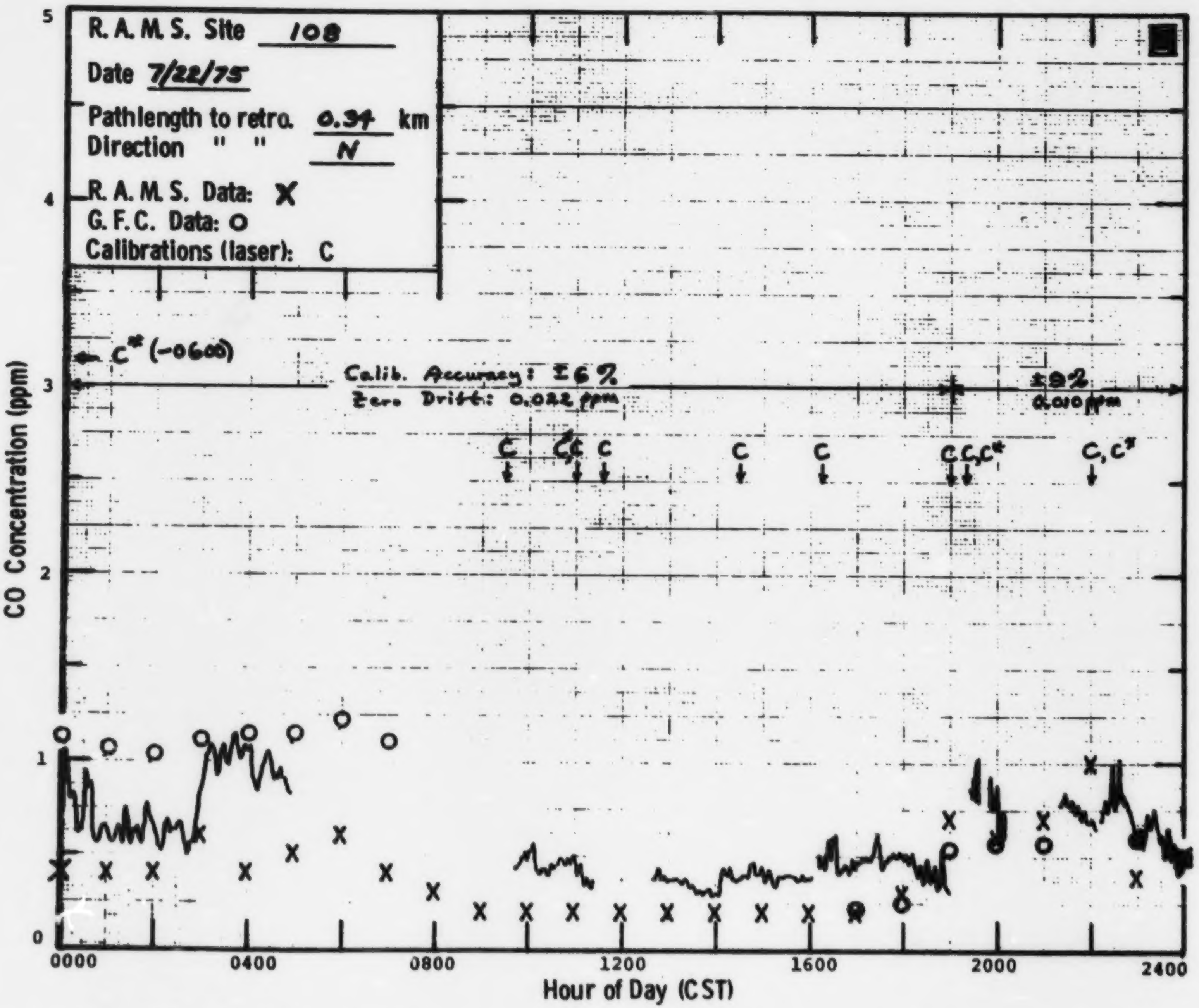

R. A. M. S. Site 108
Date 7/17/75
Pathlength to retro. 0.66 km
Direction " " W
R. A. M. S. Data: X
G. F. C. Data: ○
Calibrations (laser): C
CALIB ACC. ← ±5% →
ZERO DRIFT ±0.024 ppm
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400

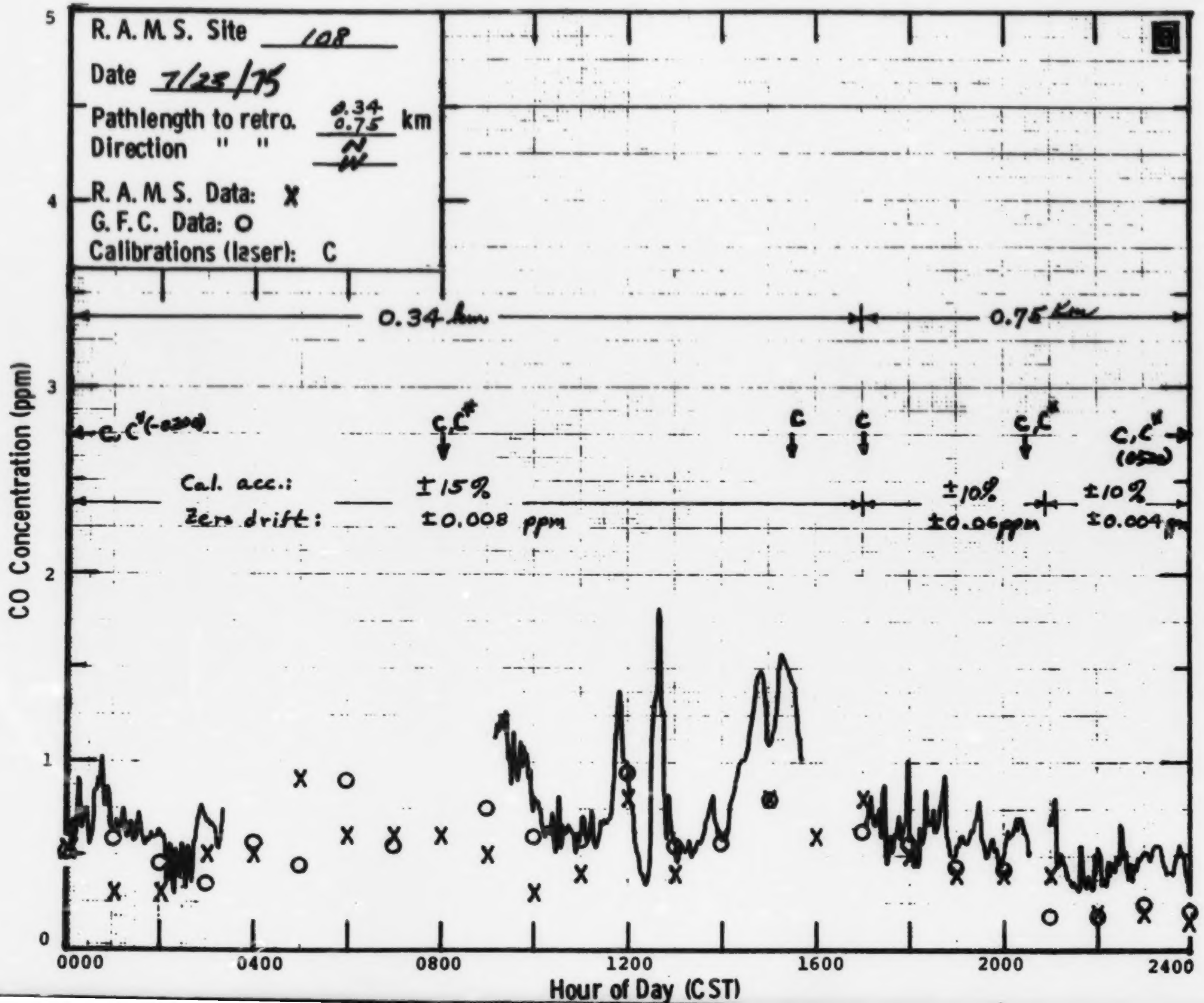

R. A. M. S. Site 108
Date 7/18/75
Pathlength to retro. 0.2 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Laser Calibration Accuracy: ±10%
Zero Drift: < 0.03 ppm
Wind velocity calibration: 5 m/sec from SW
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400
C
C
C
C
C
C
C
C
C
C
C

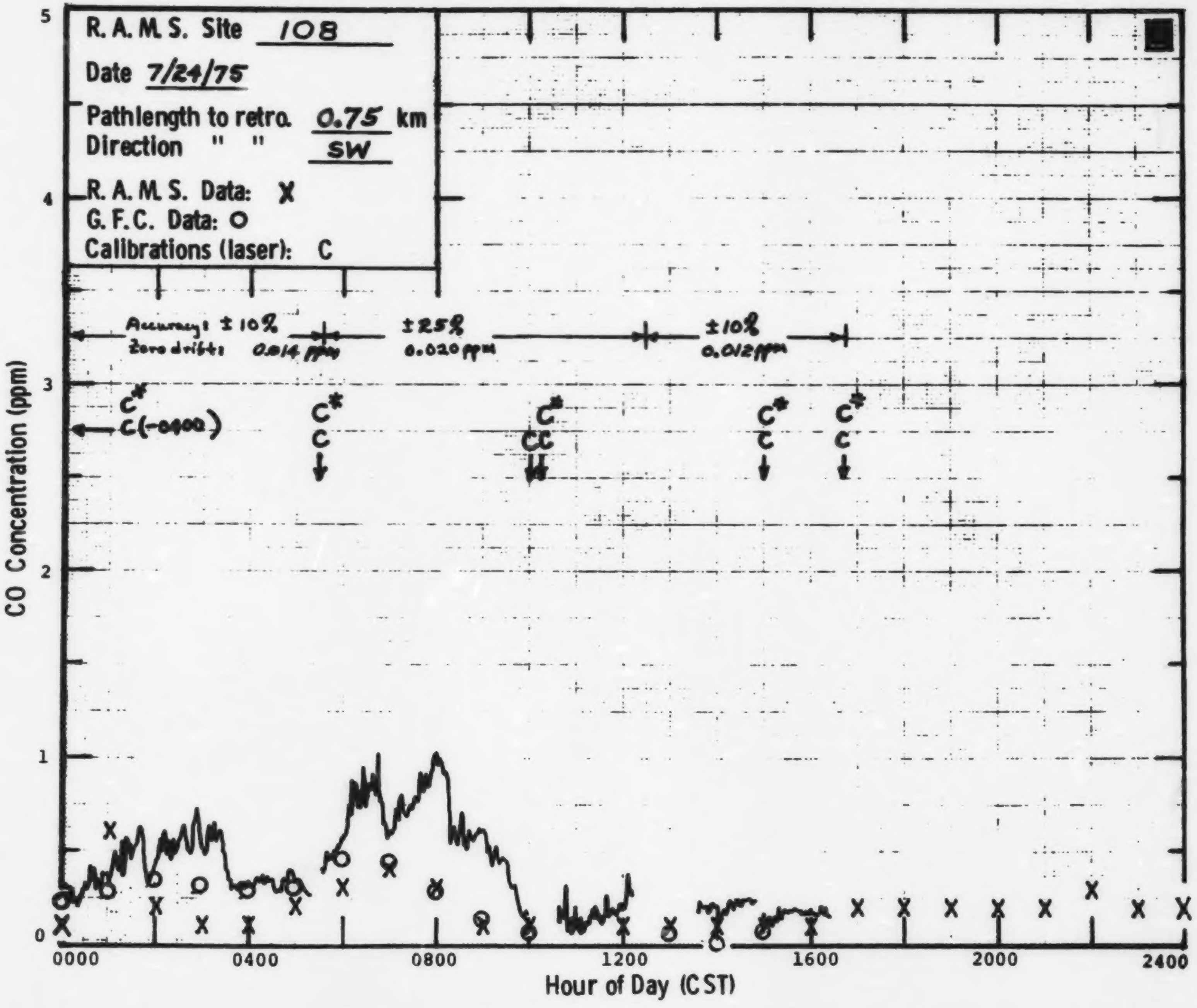

R. A. M. S. Site 108
Date 7/19/75
Pathlength to retro. 0.2 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Calib. Accuracy = ±8%
Zero Drift < 0.02 ppm
±2.5%
0.0 ppm
C,C
C
C
CC
C
C C
C
C 2438
C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400

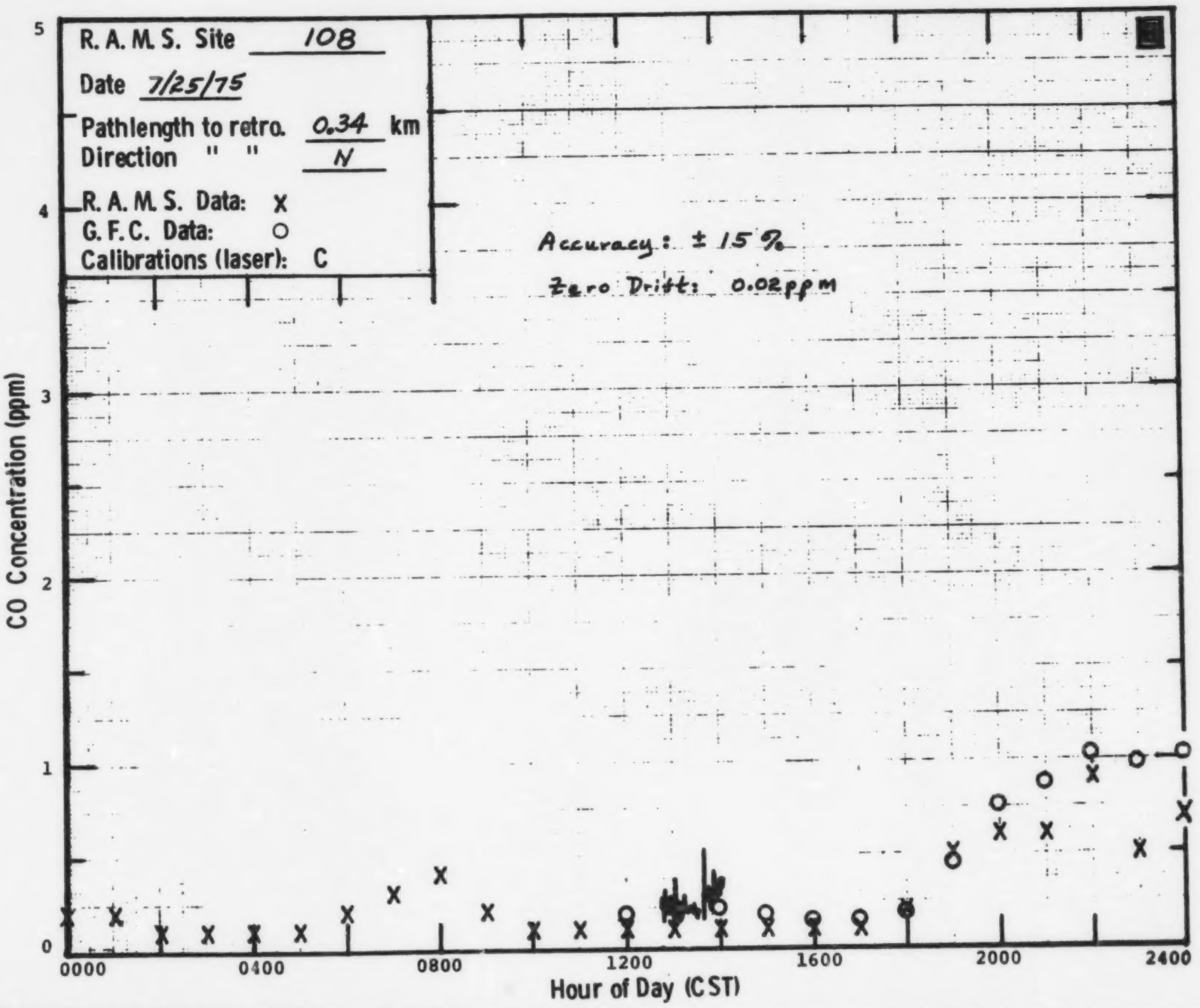

R. A. M. S. Site 108
Date 7/20/75
Pathlength to retro. 0.2 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Calib. Accuracy: ± 8%
Zero Drift: 0.00 ppm
± 16%
0.00ppm
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)

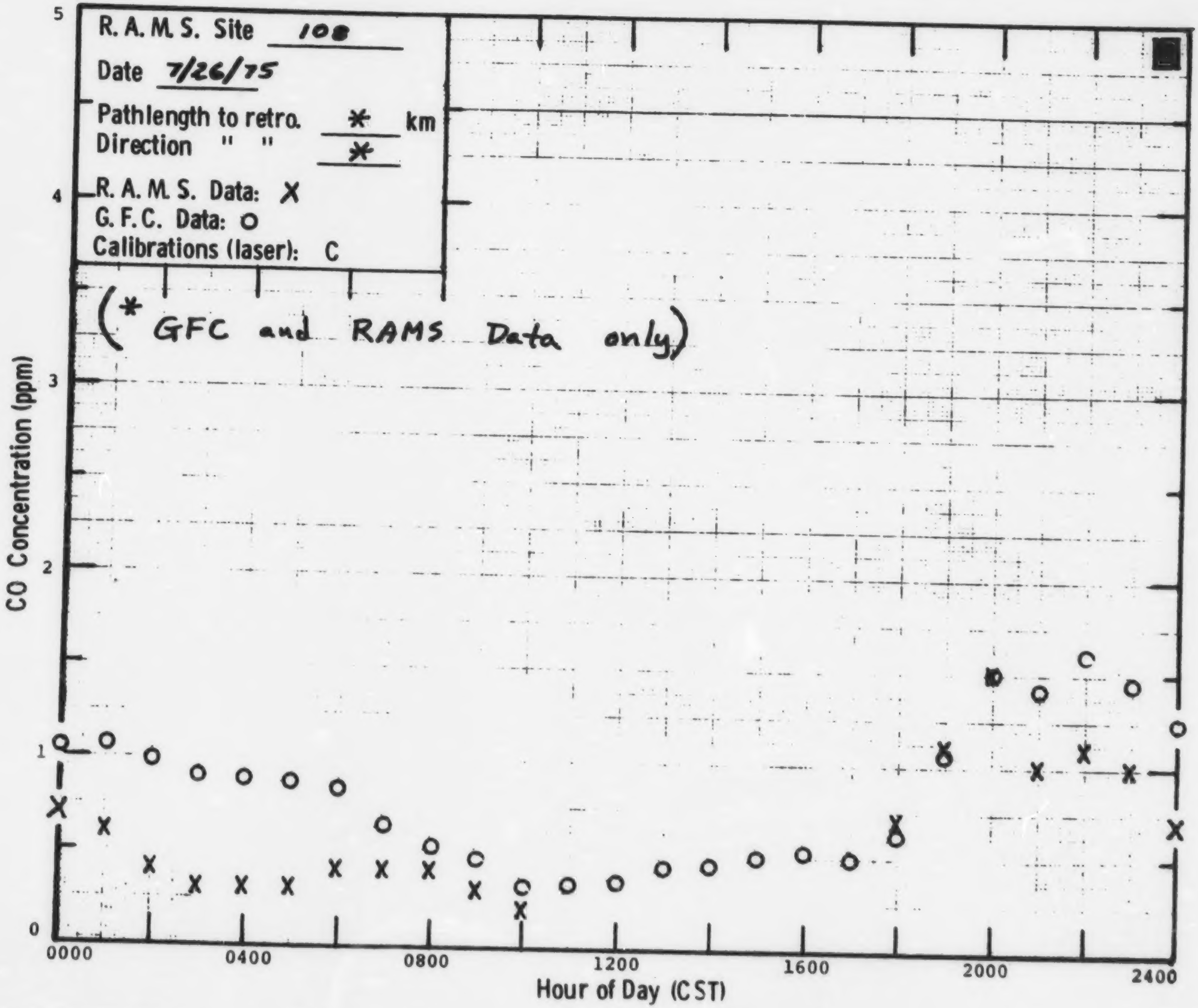

R. A. M. S. Site 108
Date 7/21/75
Pathlength to retro. 0.34 0.2 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Calib. Accuracy:
Zero Drift:
(0.2 km)
±15%
0.00 ppm
(0.34 km)
±18%
0.00 ppm
C
C*
C
C
C*
0900 → C (7/22/75)
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)

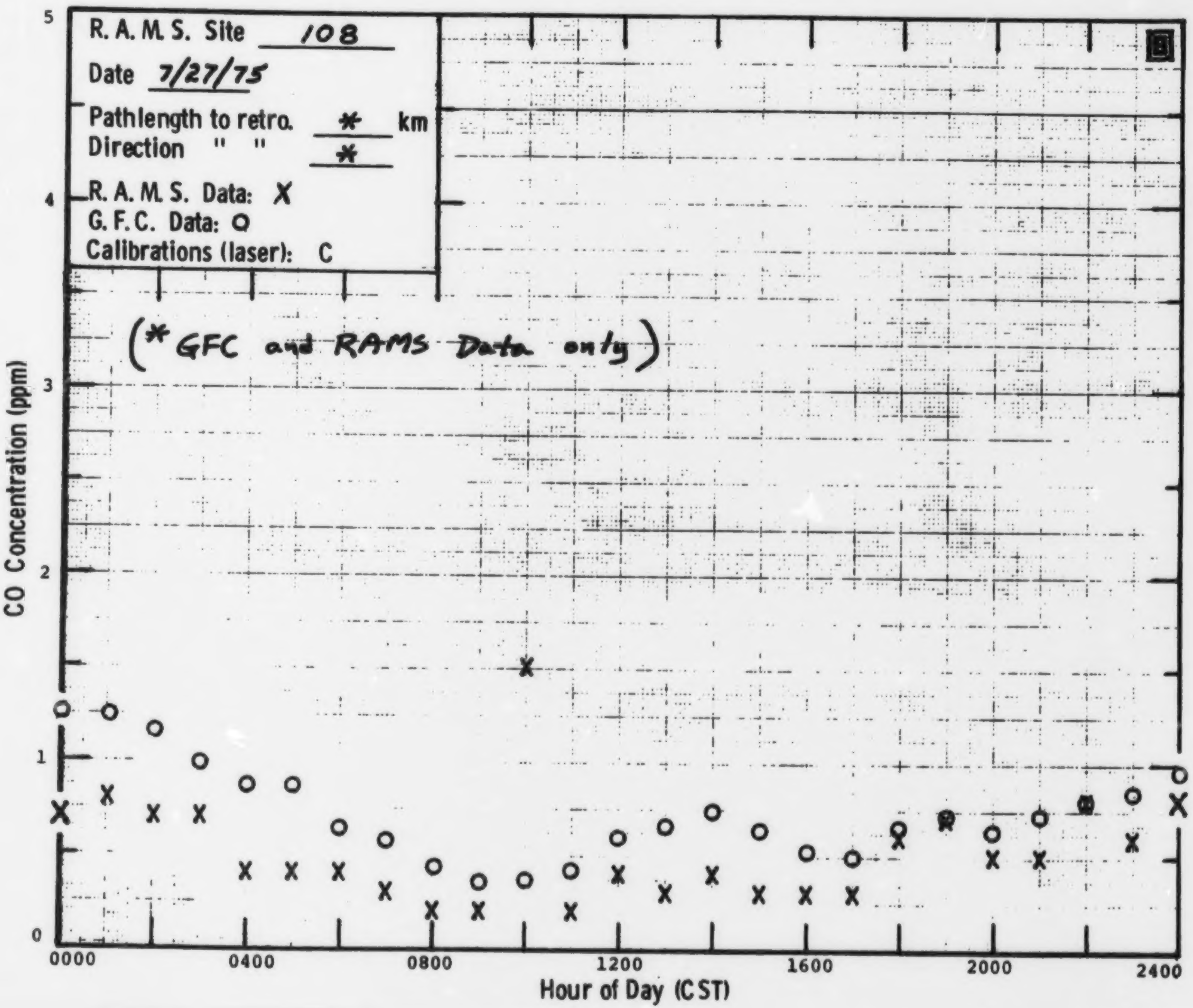

R. A. M. S. Site 108
Date 7/22/75
Pathlength to retro. 0.34 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
C* (-0600)
Calib. Accuracy: ±6%
Zero Drift: 0.022 ppm
±9%
0.010 ppm
C
C,C
C
C
C
C,C,C*
C,C*
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400

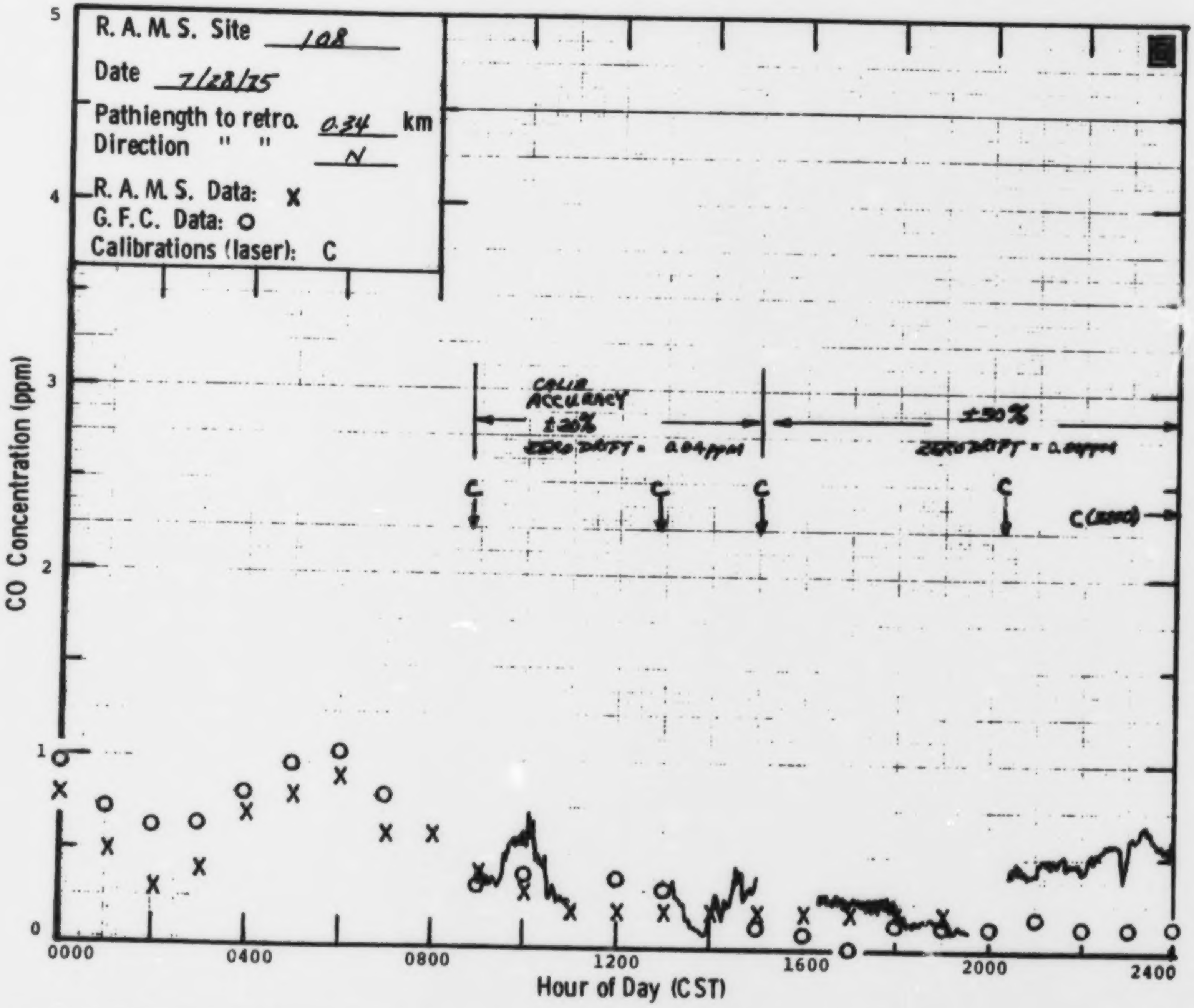

R. A. M. S. Site 108
Date 7/23/75
Pathlength to retro. 0.34 0.75 km
Direction " " N W
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
0.34 km
0.75 Km
C, C*(-0200)
C, C*
C
C
C, C*
C, C* (0500)
Cal. acc.:
Zero drift:
± 15%
±0.008 ppm
±10%
±0.06ppm
±10%
±0.004 ppm
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400

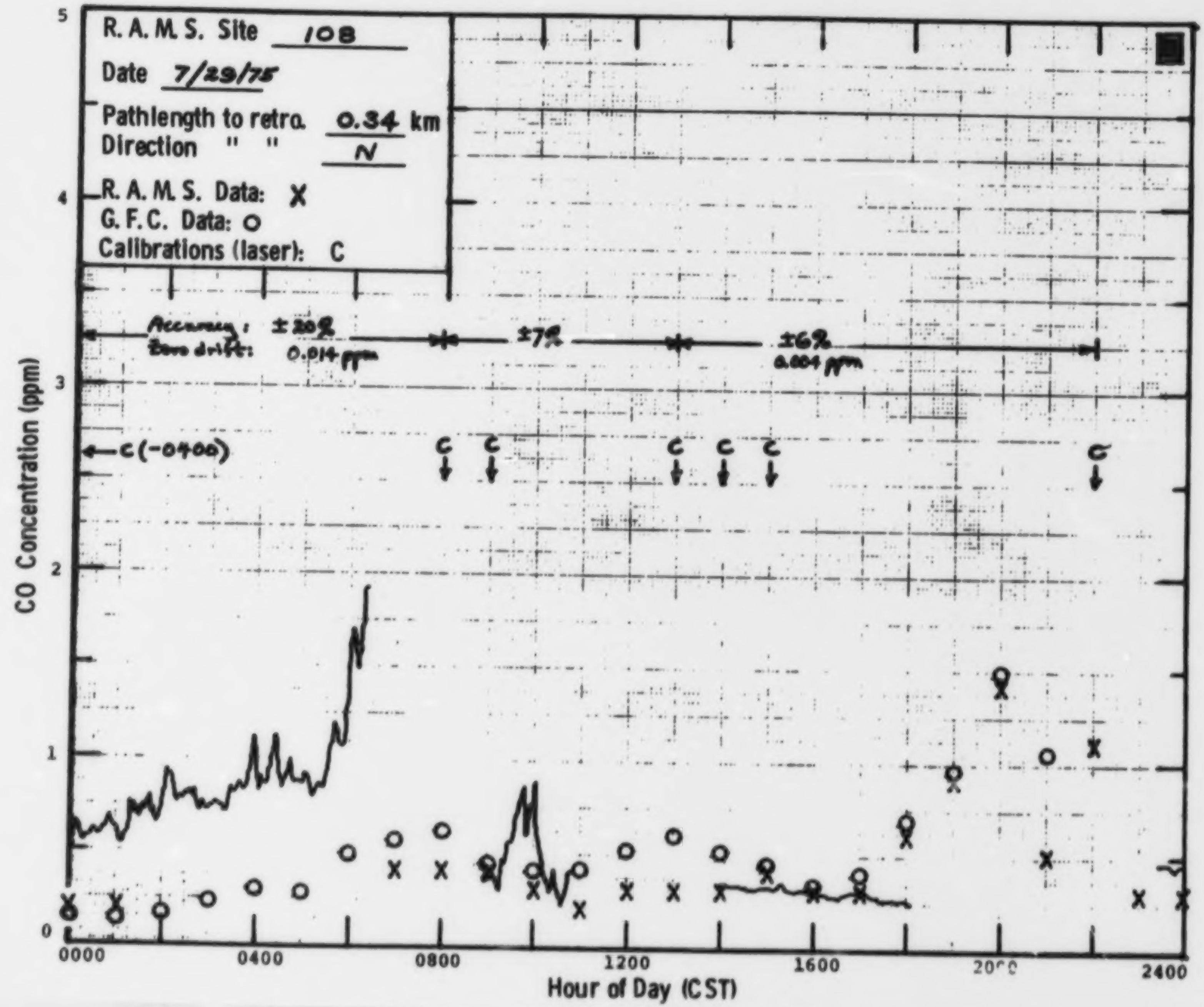
R. A. M. S. Site 108
Date 7/24/75
Pathlength to retro. 0.75 km
Direction " " SW
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Accuracy: ± 10%
Zero drift: 0.014 ppm
± 25%
0.020 ppm
± 10%
0.012 ppm
C*
C(-0400)
C*
C
C*
CC
C*
C
C*
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)

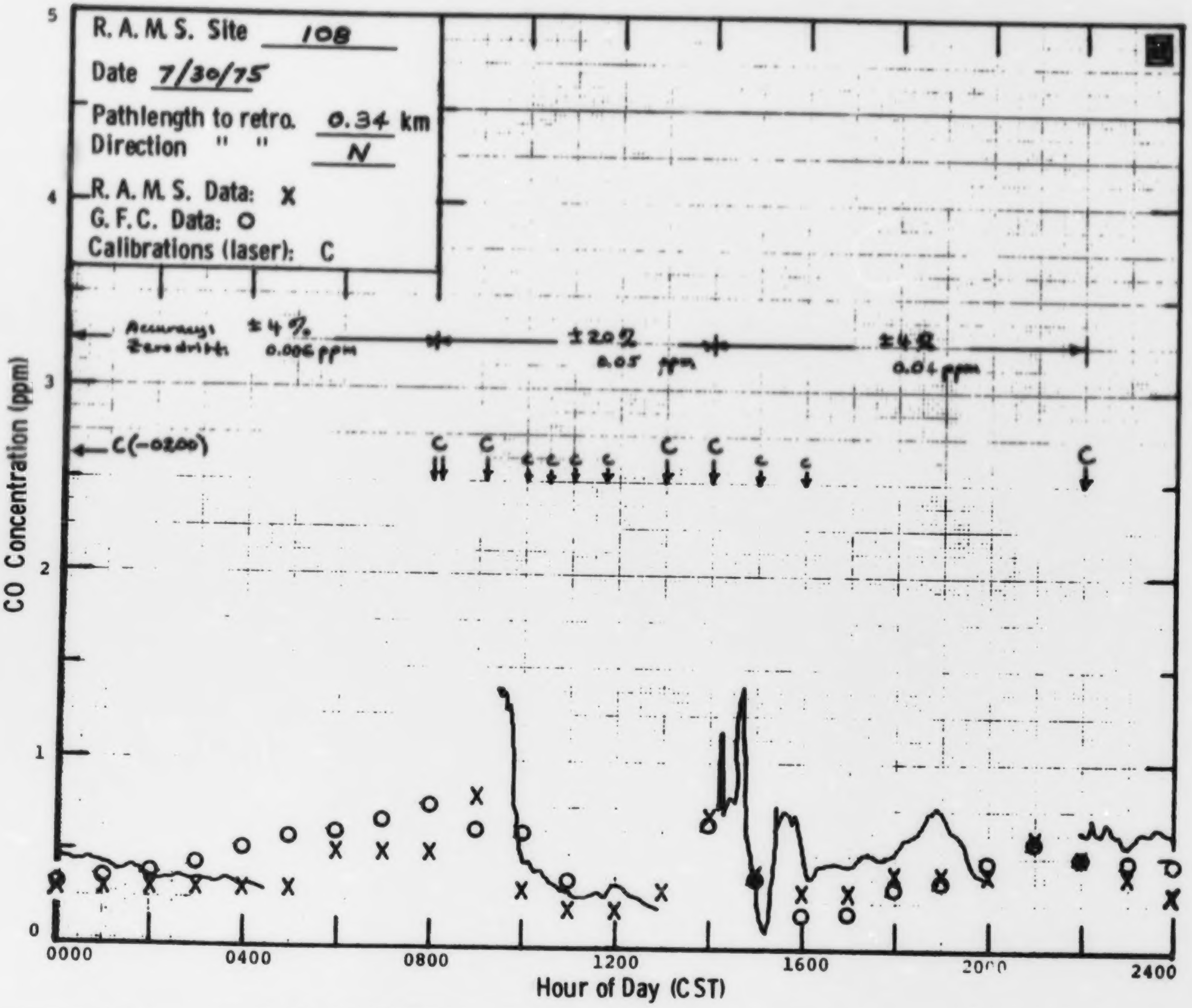

R. A. M. S. Site 108
Date 7/25/75
Pathlength to retro. 0.34 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Accuracy: ± 15 %
Zero Drift: 0.02 ppM
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 108
Date 7/26/75
Pathlength to retro. * km
Direction " " *
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
(* GFC and RAMS Data only)
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 108
Date 7/27/75
Pathlength to retro. * km
Direction " " *
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
(*GFC and RAMS Data only)
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 108
Date 7/28/75
Pathlength to retro. 0.34 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
CALIB ACCURACY ±20%
ZERO DRIFT = 0.04 ppm
±50%
ZERO DRIFT = 0.04 ppm
C
C
C
C
C (2330)
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 108
Date 7/29/75
Pathlength to retro. 0.34 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Accuracy: ±20%
Zero drift: 0.014 ppm
±7%
±6%
0.004 ppm
C(-0400)
C
C
C
C
C
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)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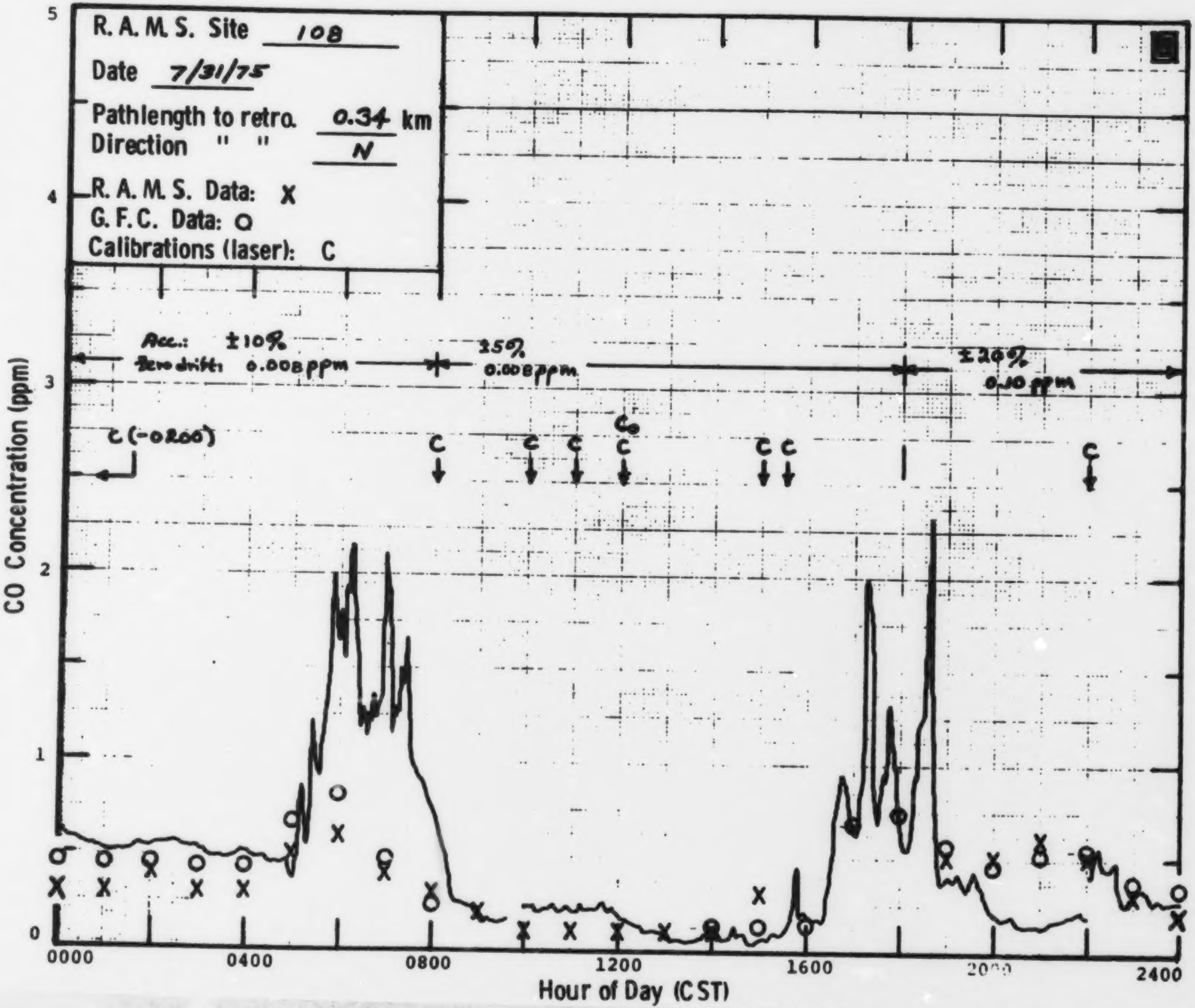
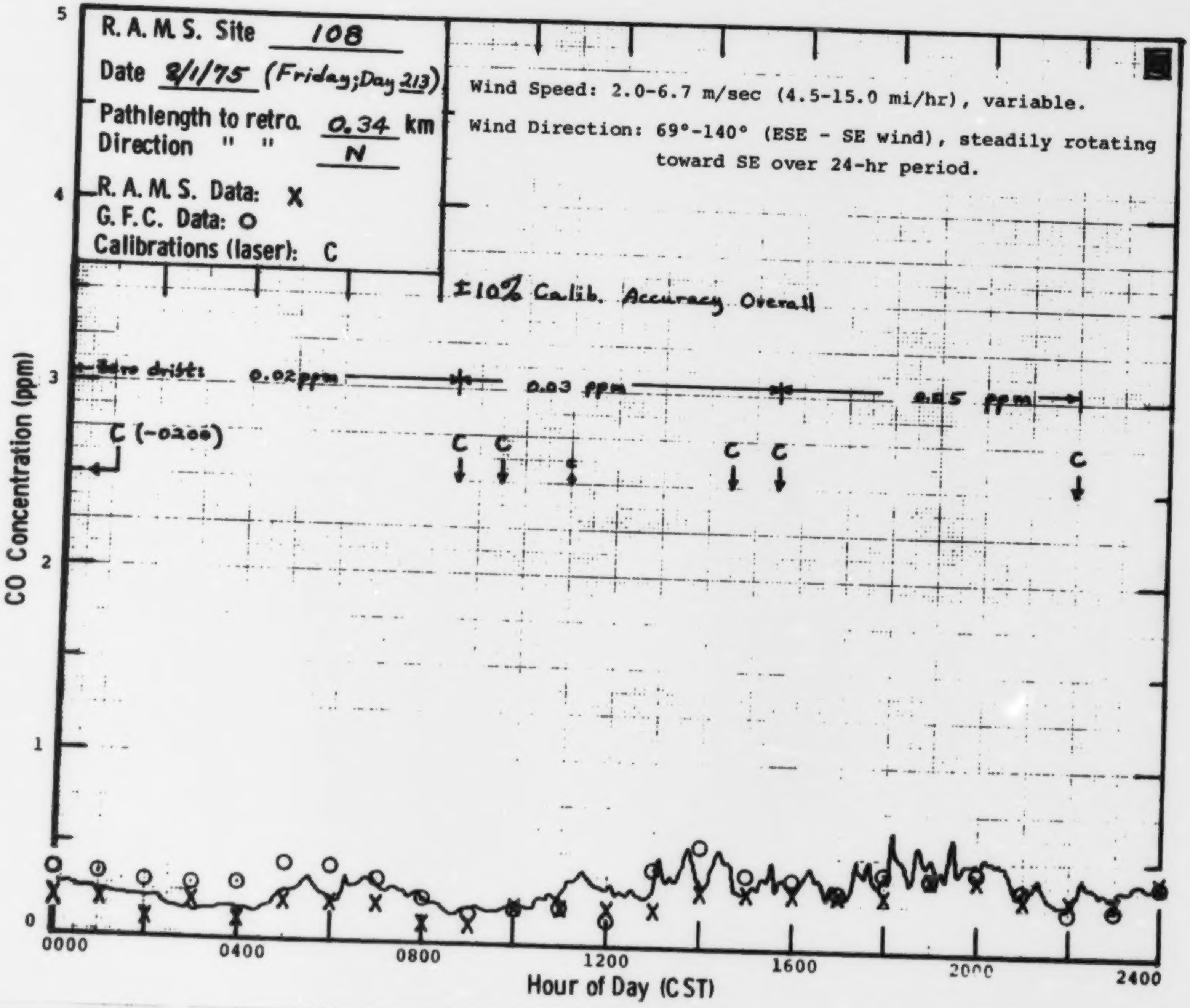
Date 7/30/75
Pathlength to retro. 0.34 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Accuracy: ±4%
Zero drift: 0.006 ppm
±20%
0.05 ppm
±4%
0.04 ppm
C(~0200)
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 108
Date 7/31/75
Pathlength to retro. 0.34 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Acc.: ±10%
Zero drift: 0.008 ppm
±5%
0.008 ppm
±20%
0.10 ppm
C (-0200)
C
C
C
Co
C
C
C
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)



R. A. M. S. Site 108

Date 8/1/75 (Friday; Day 213)

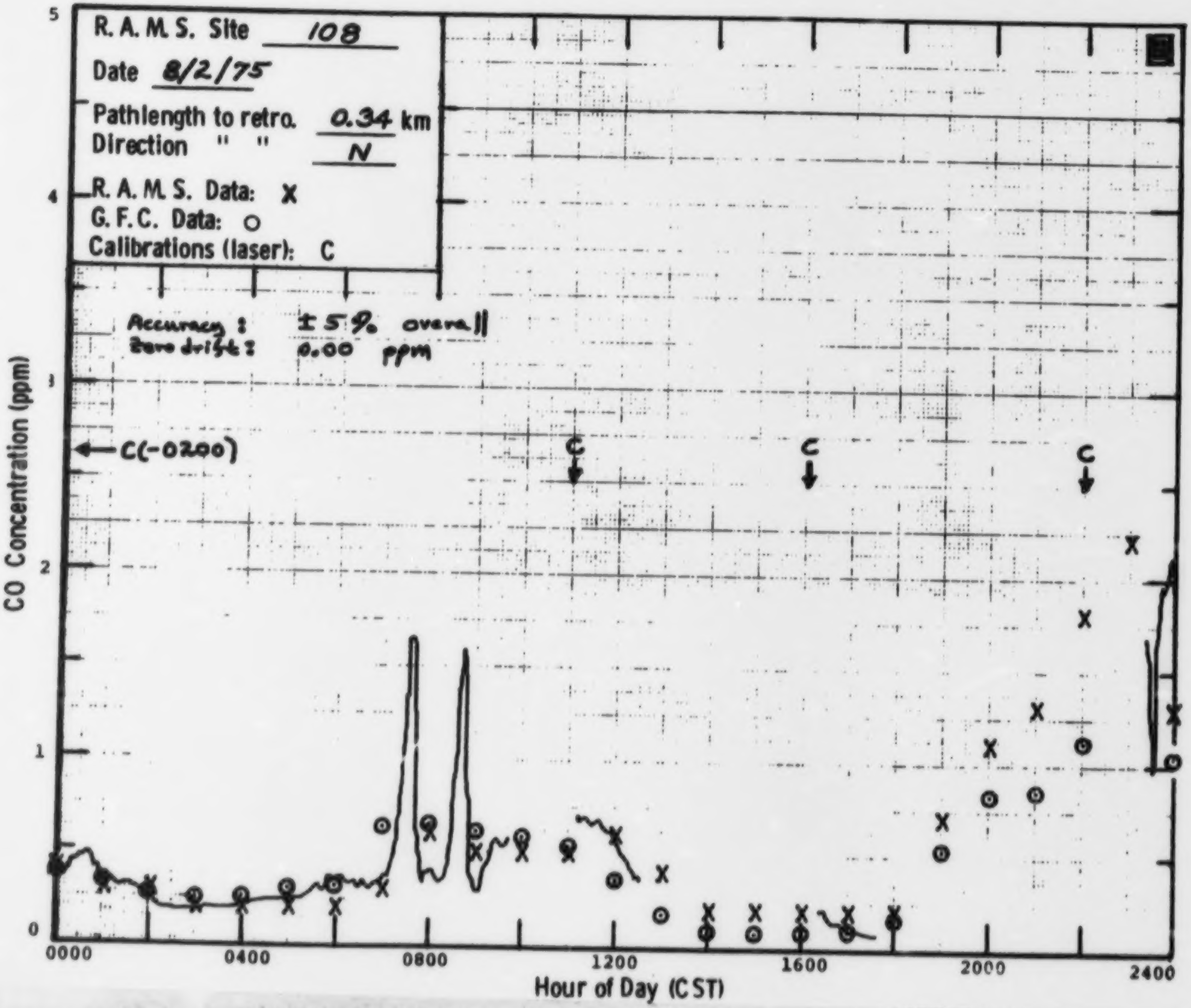
Pathlength to retro. 0.34 km
Direction " " N

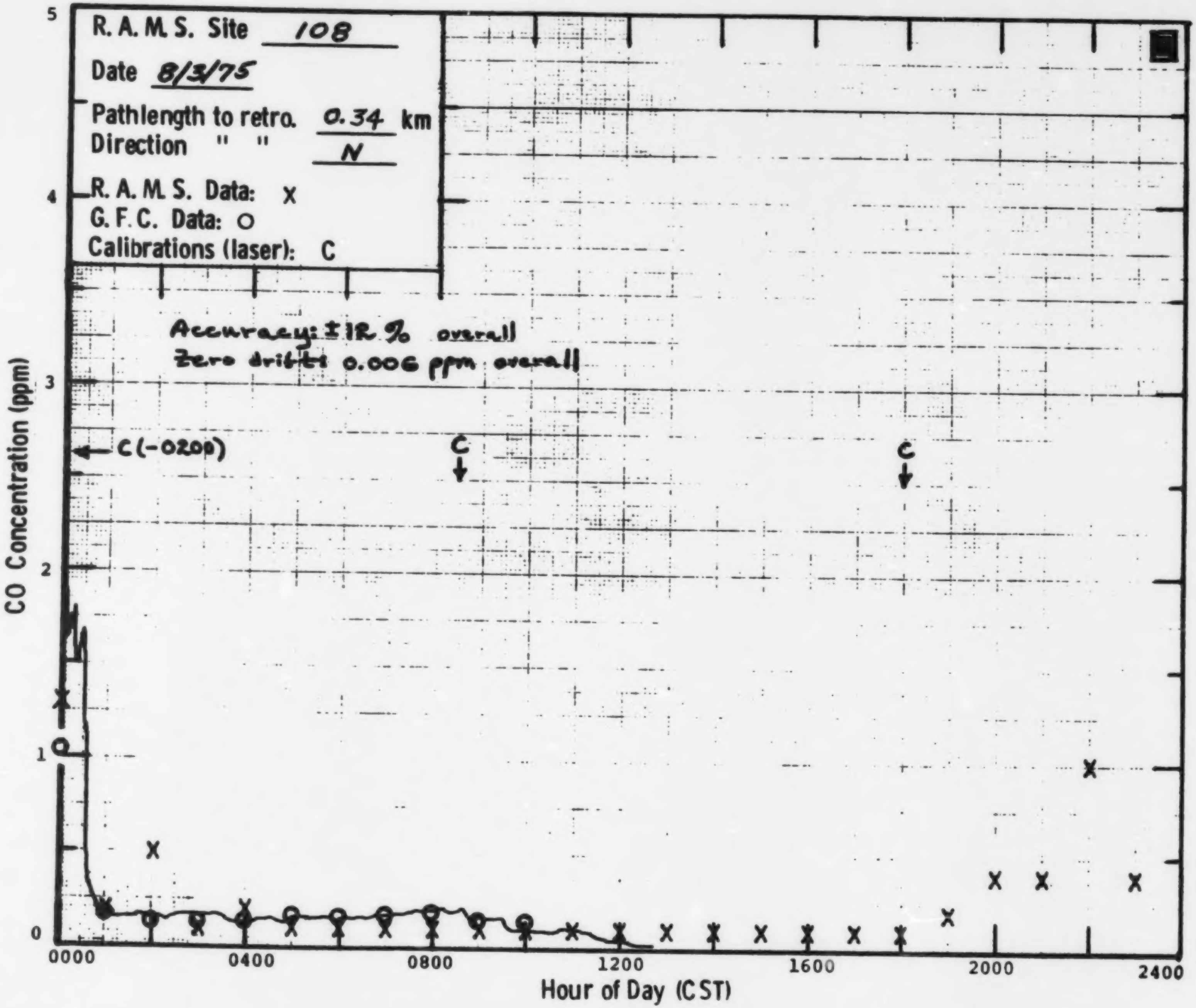
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C

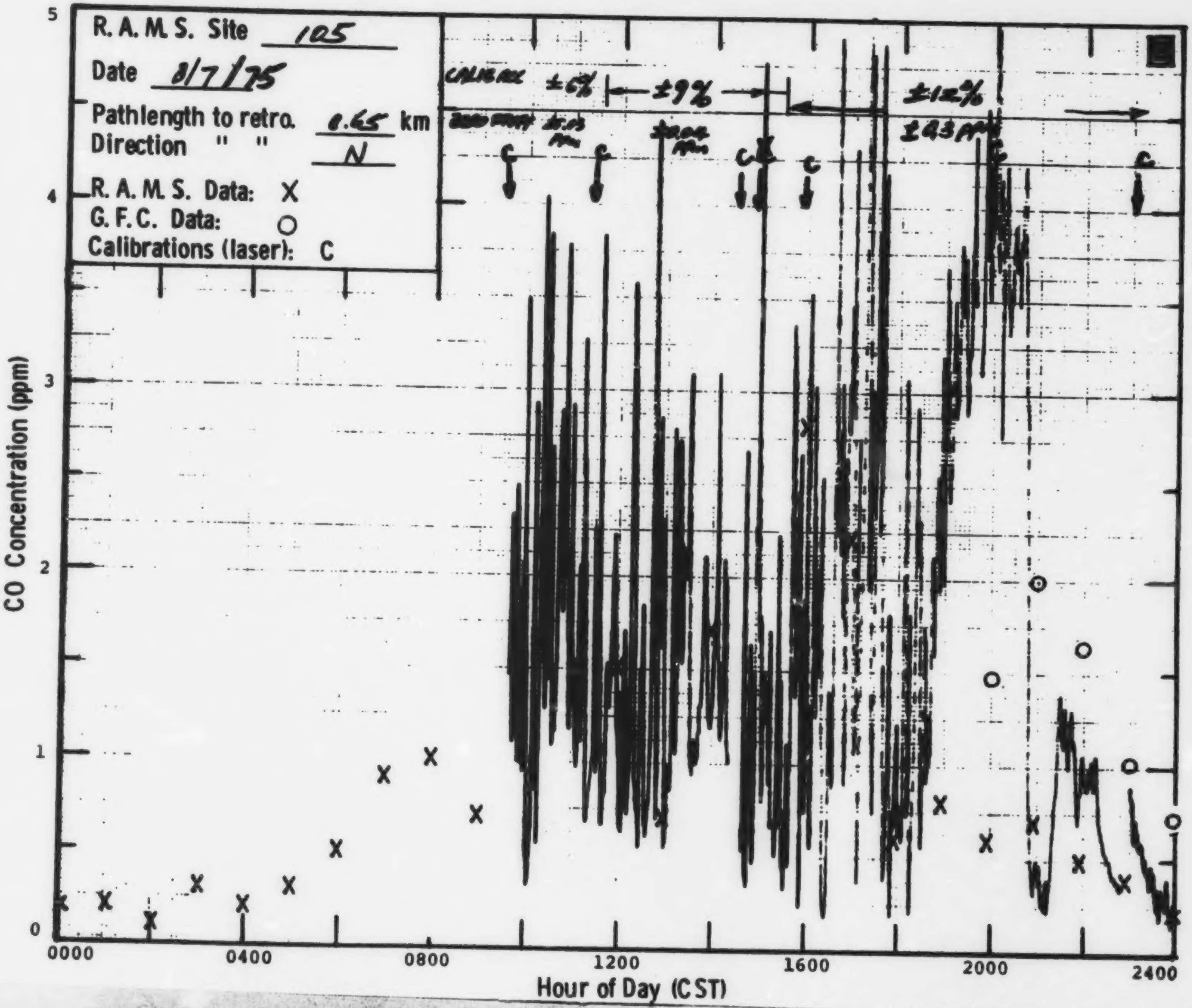
Wind Speed: 2.0-6.7 m/sec (4.5-15.0 mi/hr), variable.

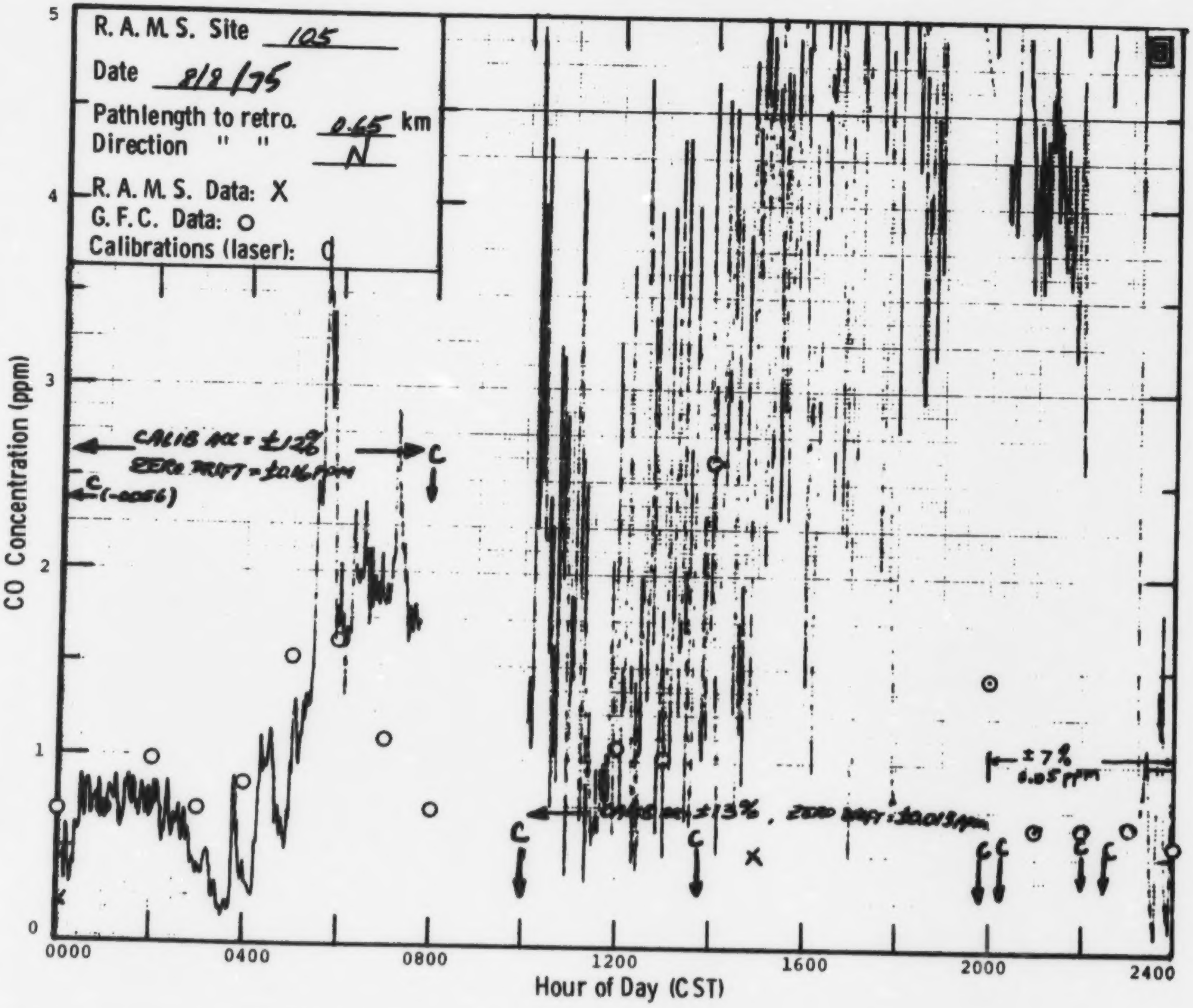
Wind Direction: 69°-140° (ESE - SE wind), steadily rotating toward SE over 24-hr period.

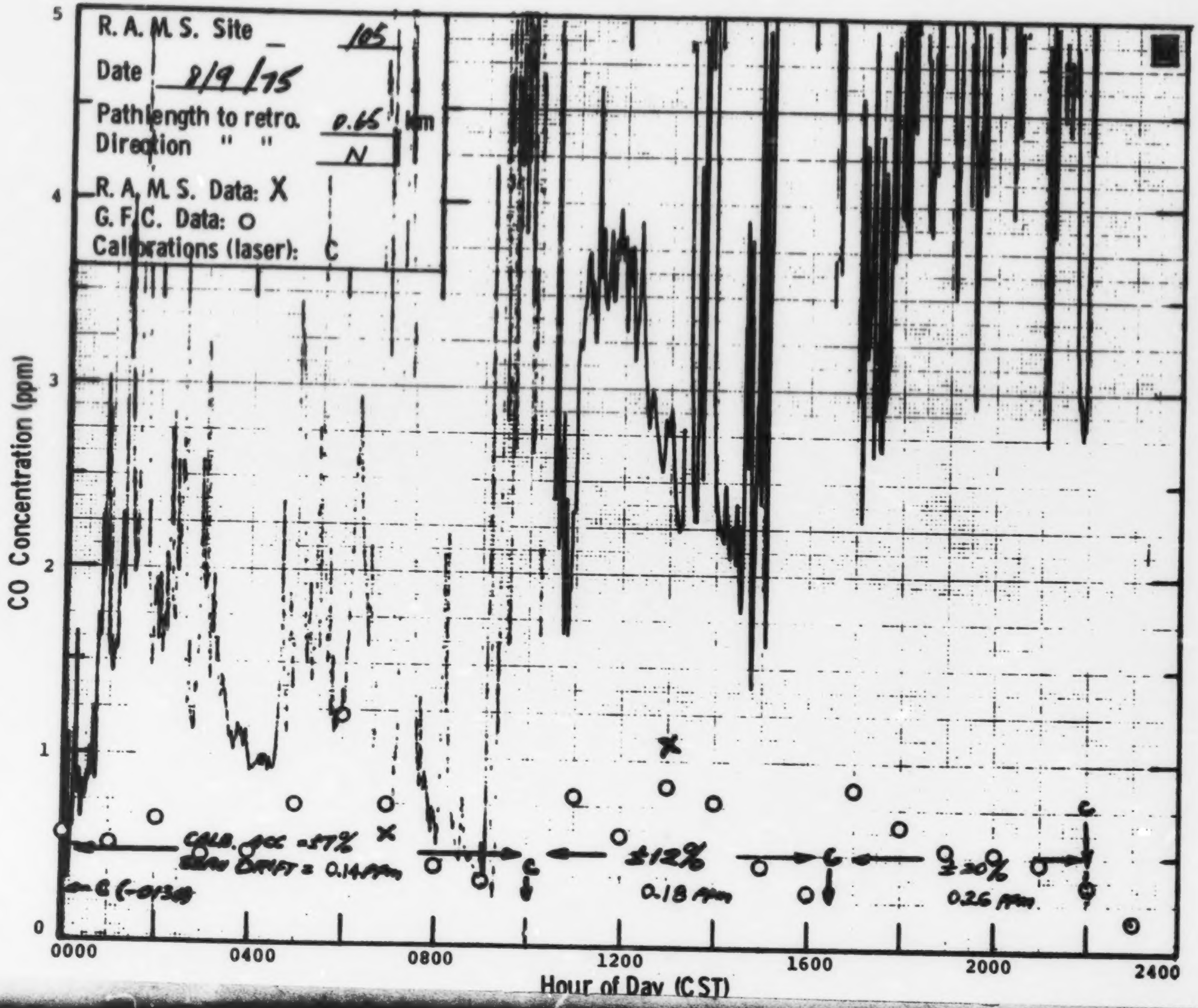
±10% Calib. Accuracy Overall

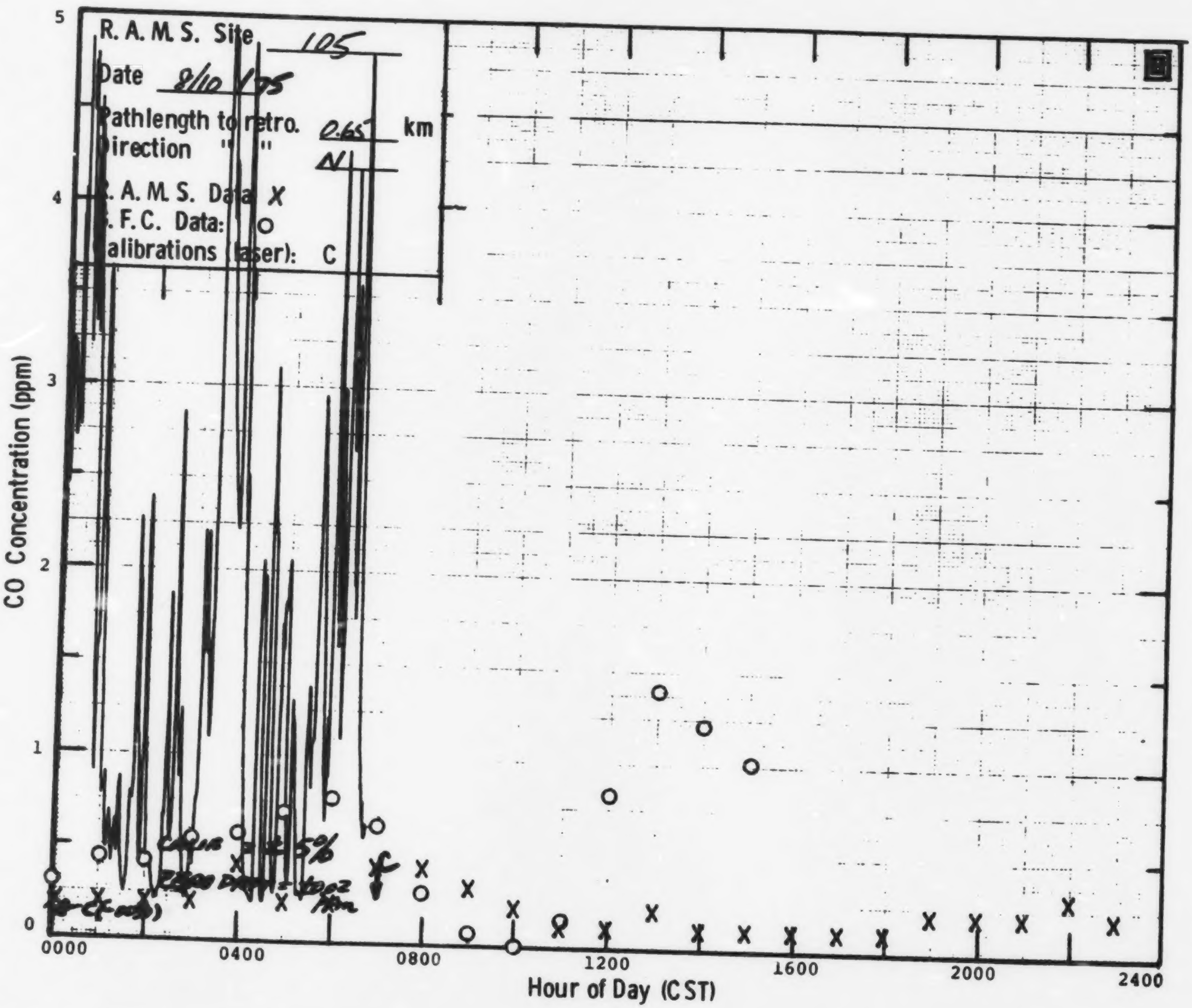

R. A. M. S. Site 108
Date 8/2/75
Pathlength to retro. 0.34 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: ○
Calibrations (laser): C
Accuracy: ±5% overall
Zero drift: 0.00 ppm
C(-0200)
C
C
C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400

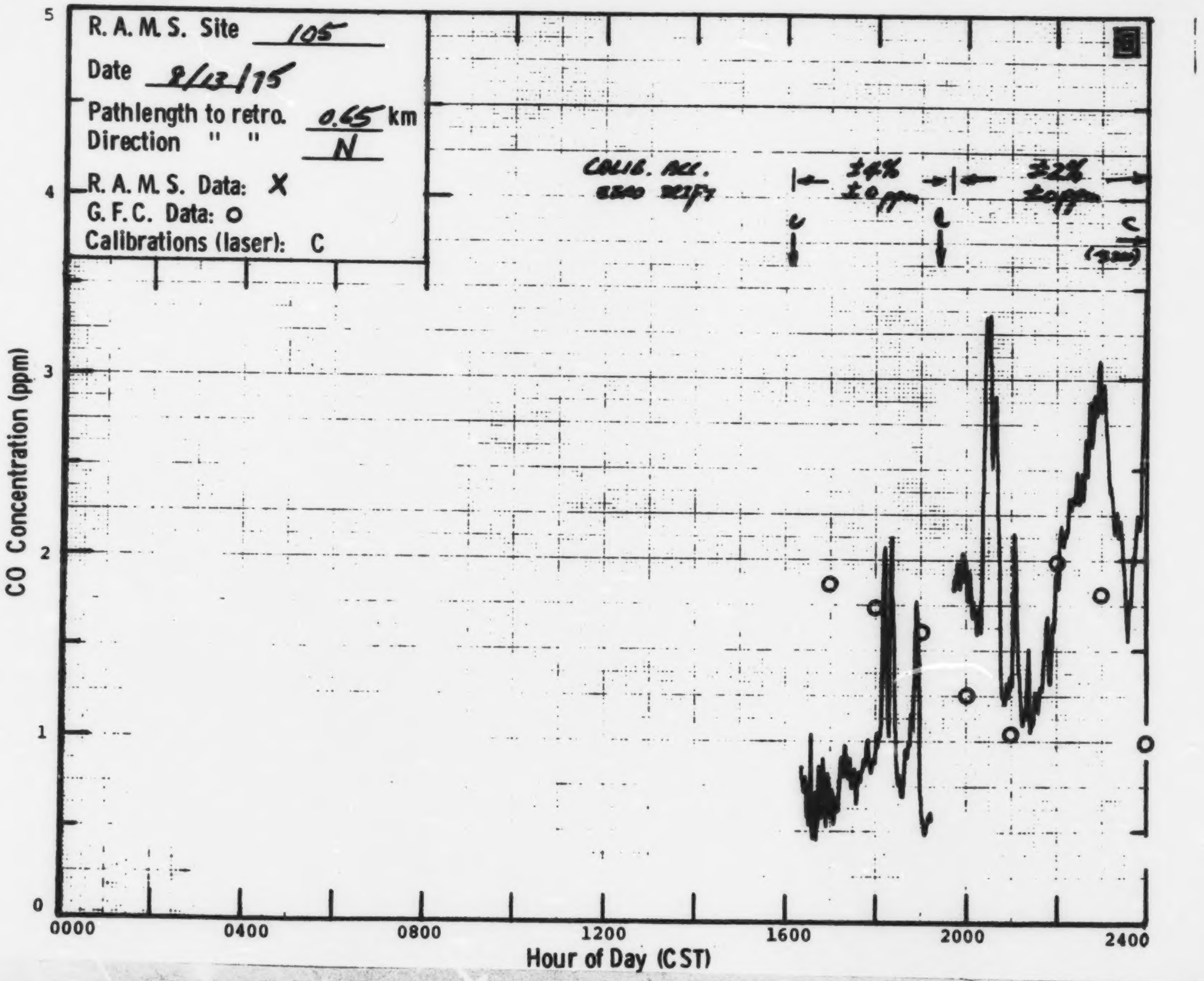

R. A. M. S. Site 108
Date 8/3/75
Pathlength to retro. 0.34 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Accuracy: ±12 % overall
Zero drift: 0.006 ppm overall
C(-0200)
C
C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400

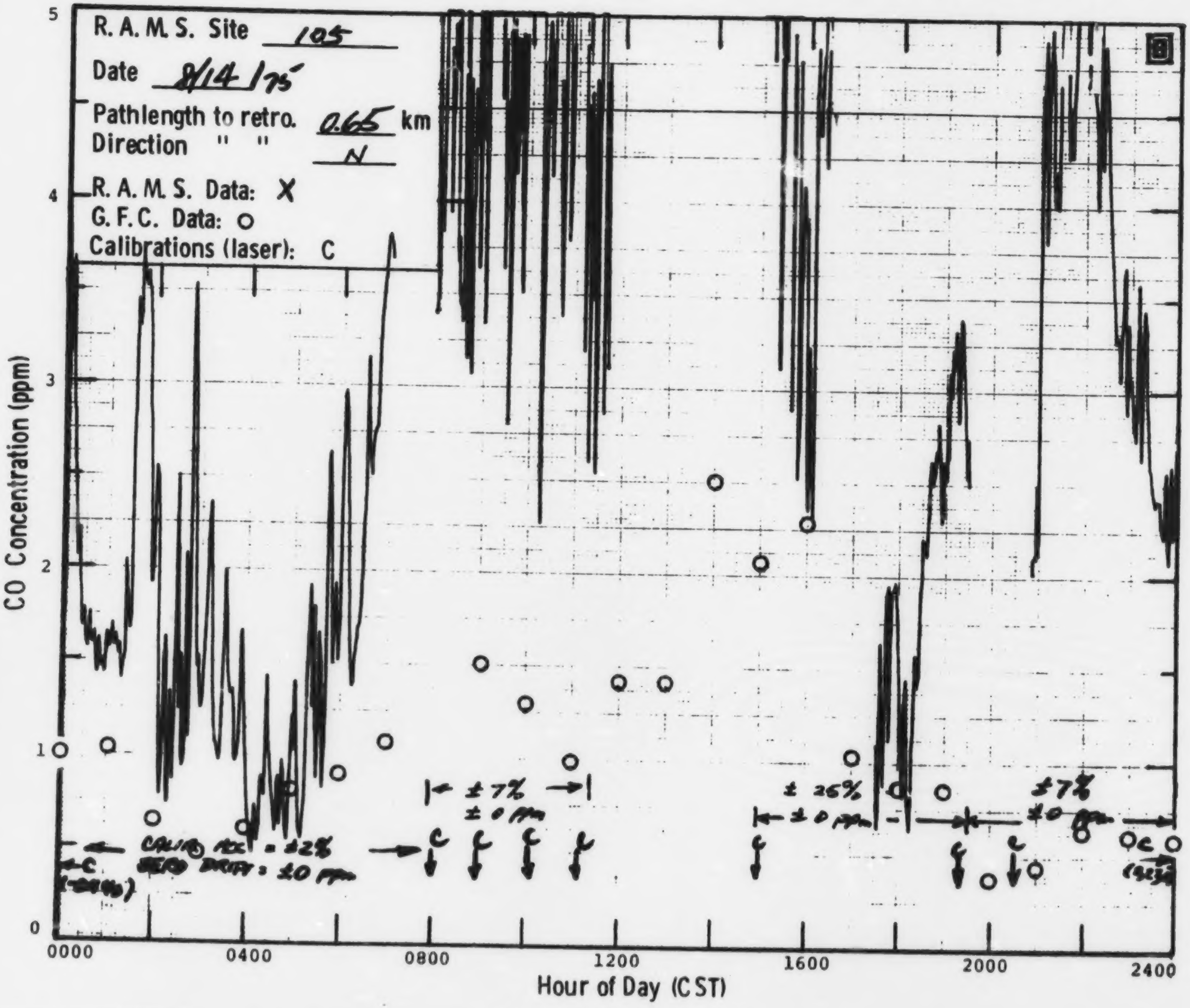

R. A. M. S. Site 105
Date 8/7/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: ○
Calibrations (laser): C
CALIBRAX ±6%
±9%
±12%
±.13 ppm
±.08 ppm
±.43 ppm
C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400

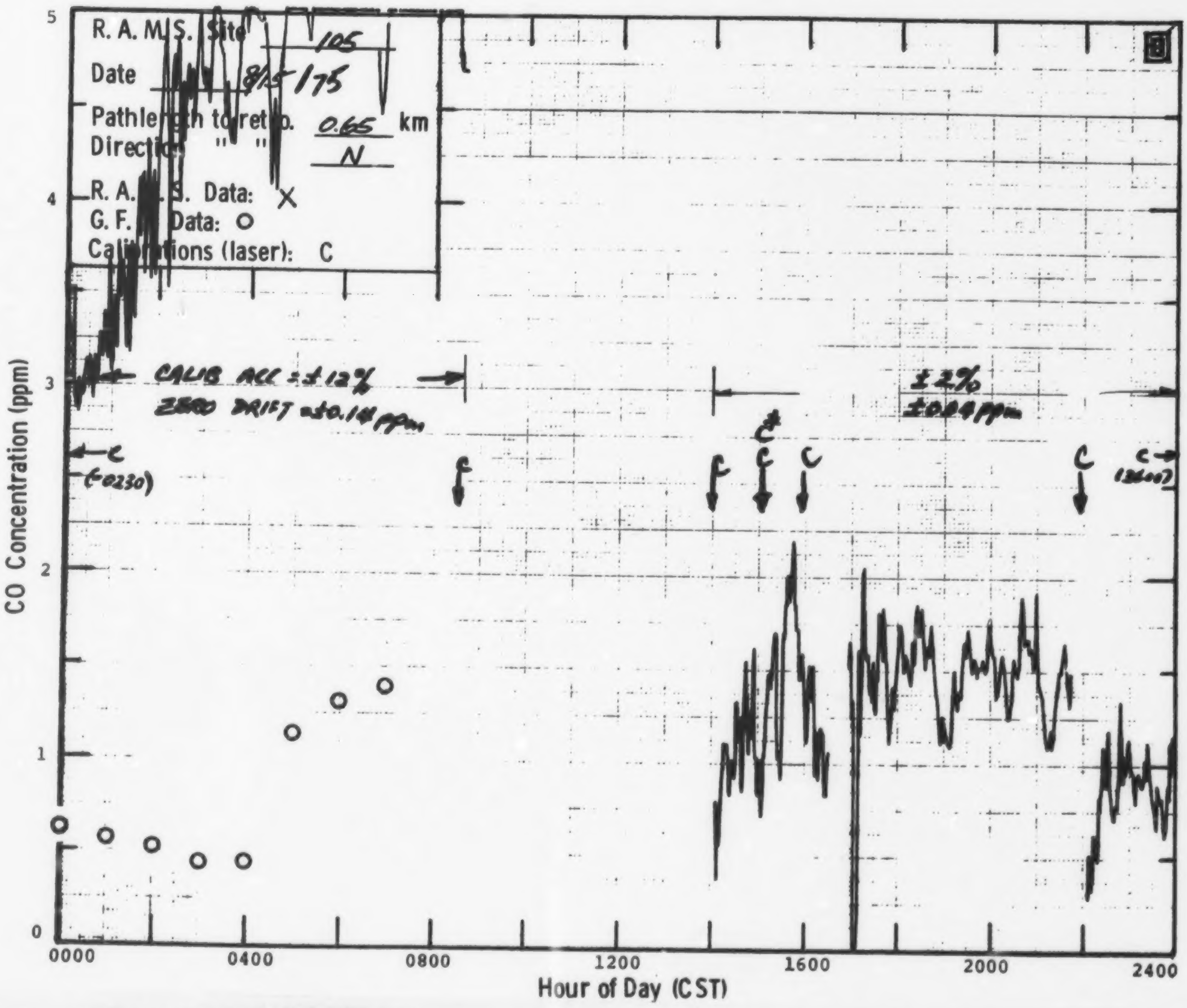

R. A. M. S. Site 105
Date 8/8/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: ○
Calibrations (laser): ¢
CALIB ACC = ±12%
ZERO DRIFT = ±0.16 ppm
C (-.0056)
C
C
C
CALIB ACC = ±13%, ZERO DRIFT = ±0.013 ppm
±7%
0.05 ppm
C C
C
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)
3

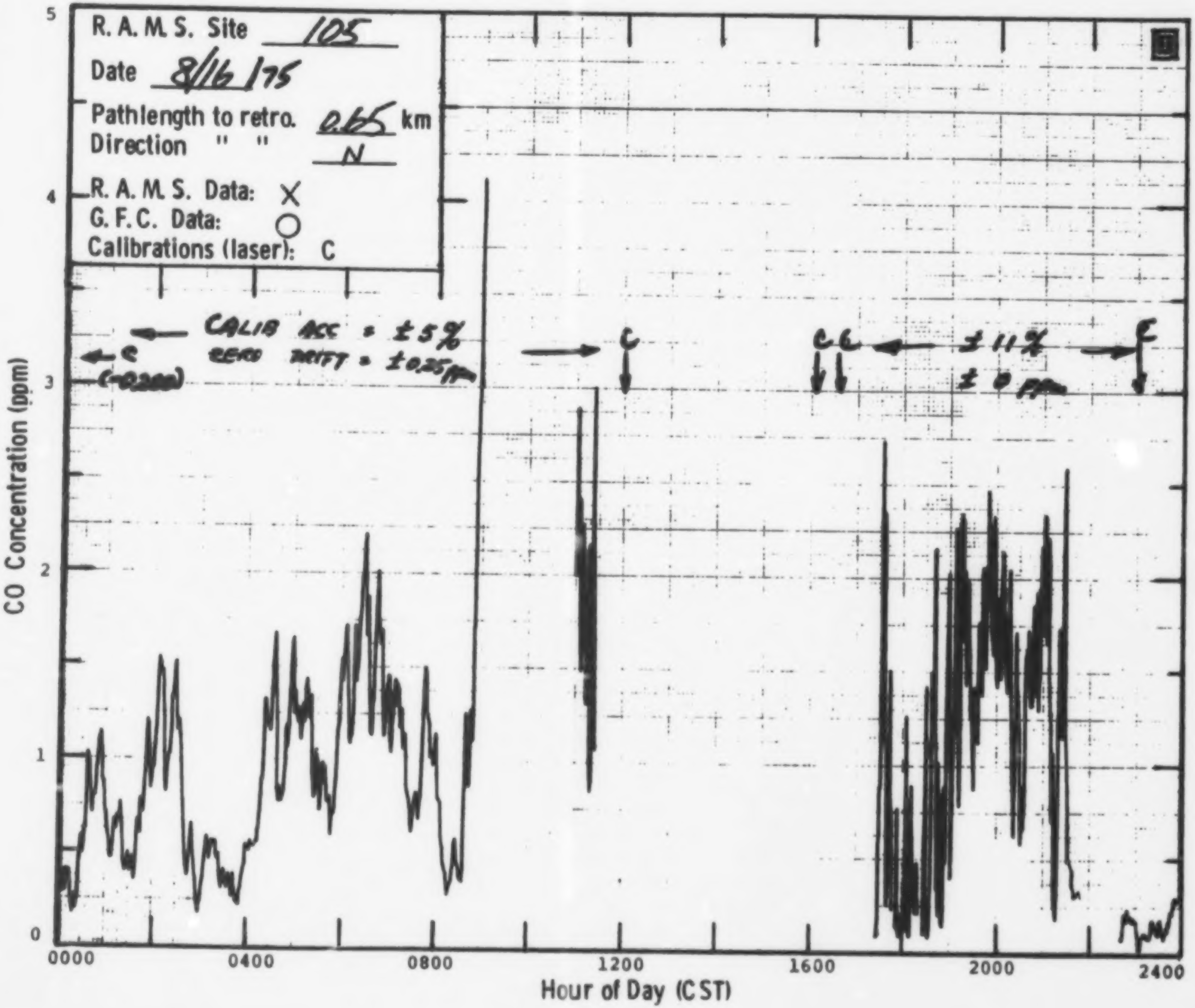

R. A. M. S. Site 105
Date 8/9/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400
C (-0130)
CALB. ACC =57%
SPAN DRIFT = 0.14 PPm
C
±12%
0.18 PPm
C
±20%
0.26 PPm
C

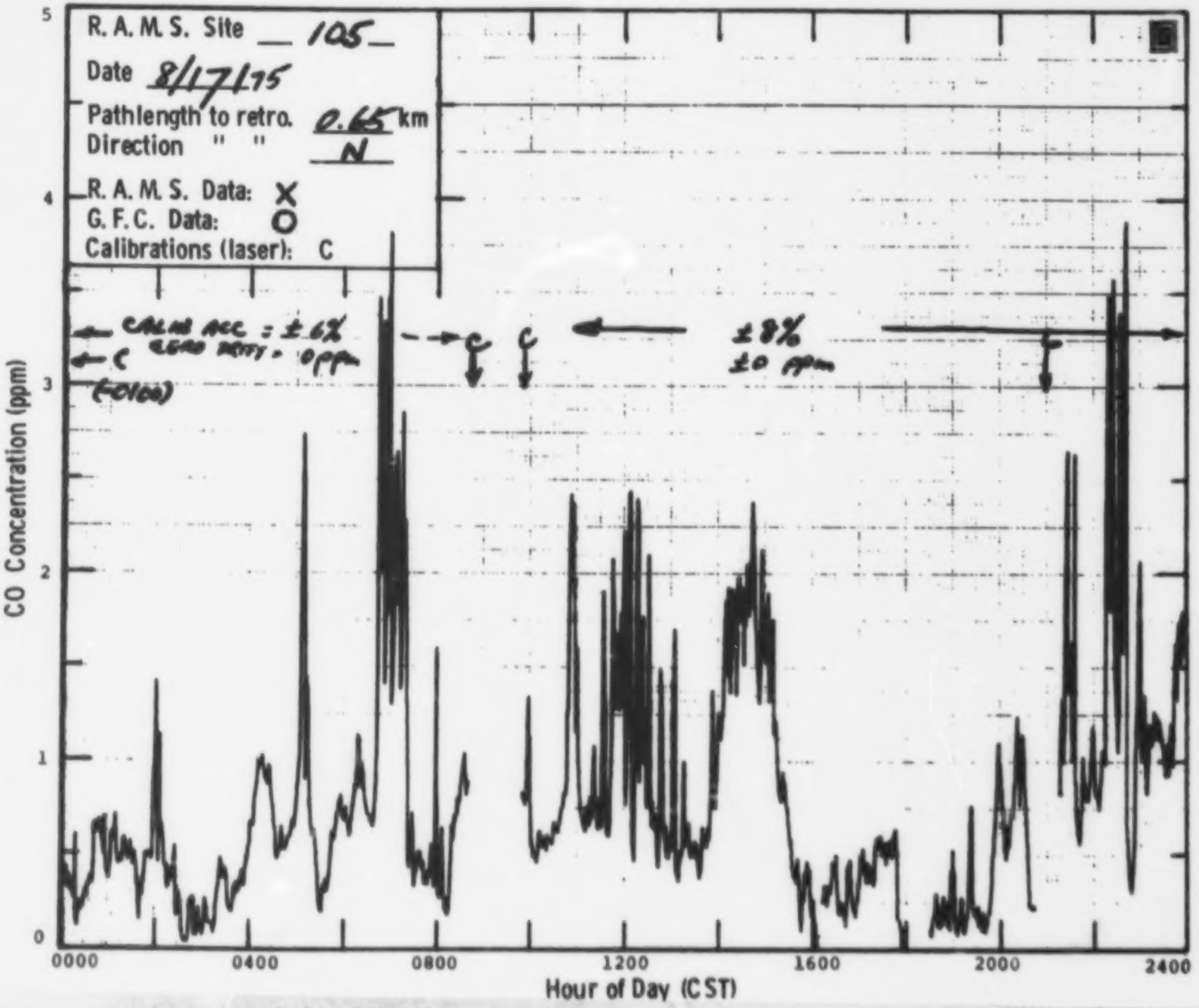

R. A. M. S. Site 105
Date 8/10/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data X
S. F. C. Data: O
Calibrations (laser): C
CALIB = ±5%
ZERO DRIFT = .002 ppm
C(-.003)
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400

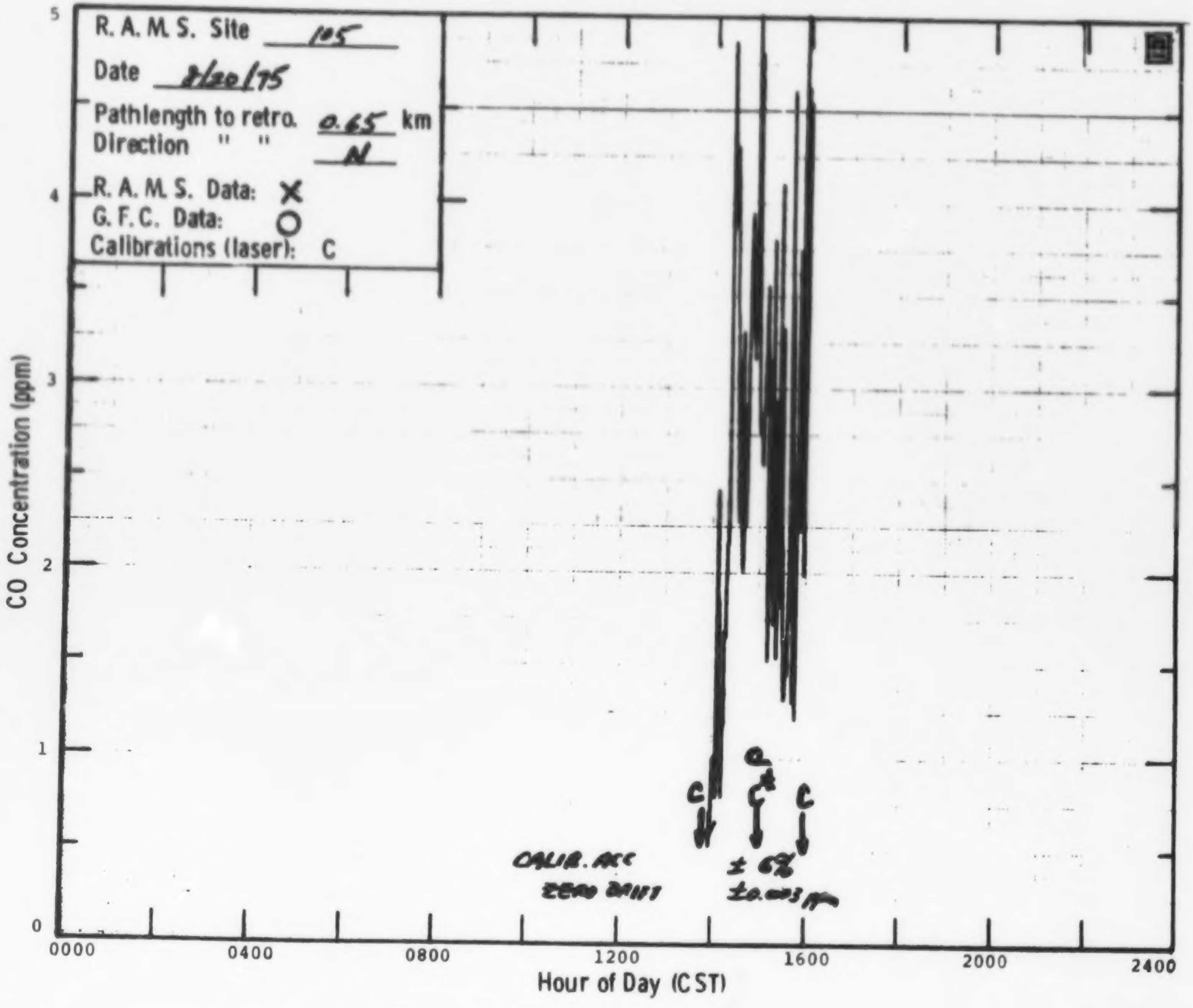

R. A. M. S. Site 105
Date 8/13/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
CALIB. ACC.
ZERO DRIFT
34%
±0 ppm
32%
±0 ppm
C
C
C
(2300)
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)

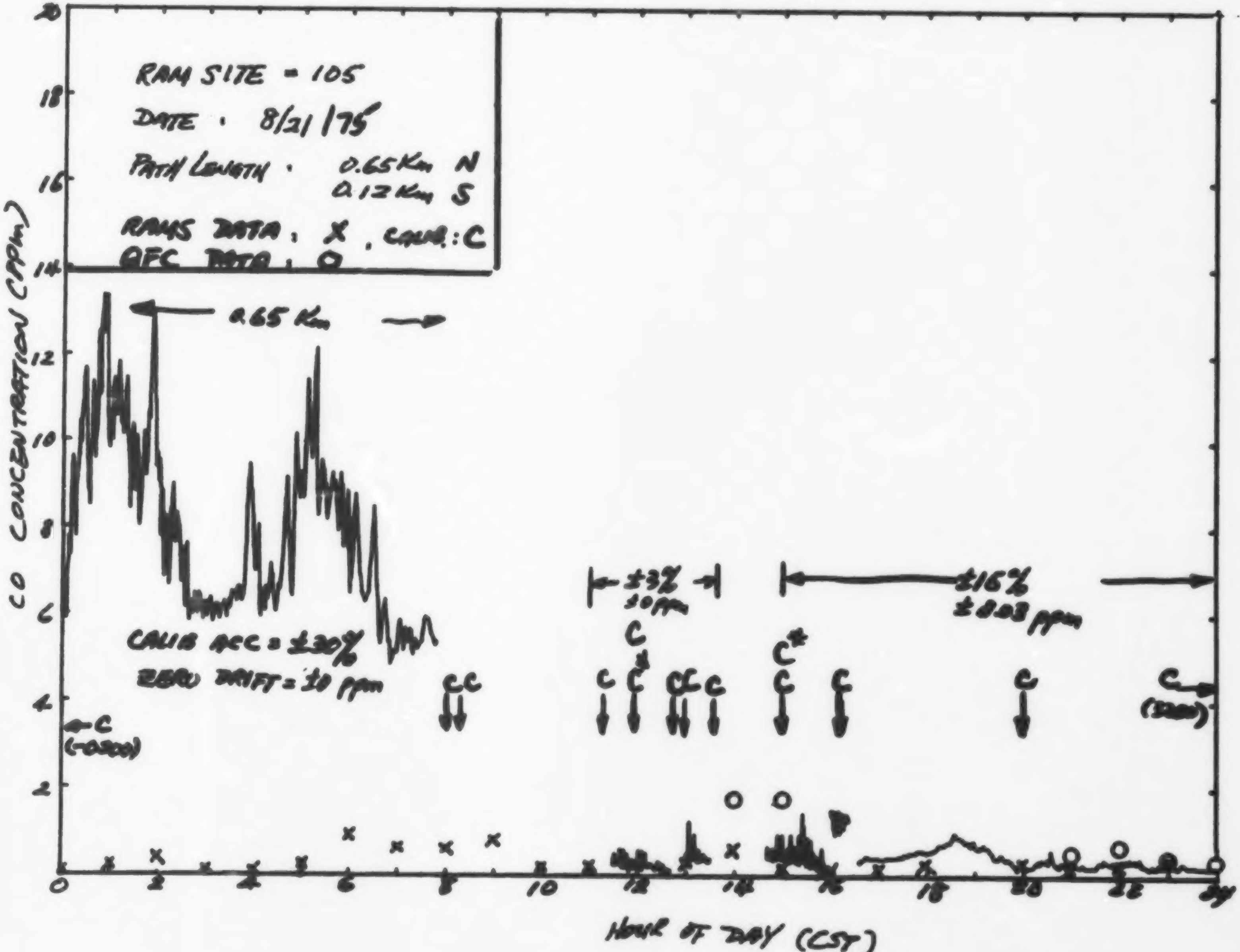

R. A. M. S. Site 105
Date 8/14/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400
CALIB ACC = ±2%
ZERO DRIFT = ±0 ppm
C
(-28%)
± 7%
± 0 ppm
± 25%
± 0 ppm
±7%
±0 ppm
C
(-32%)

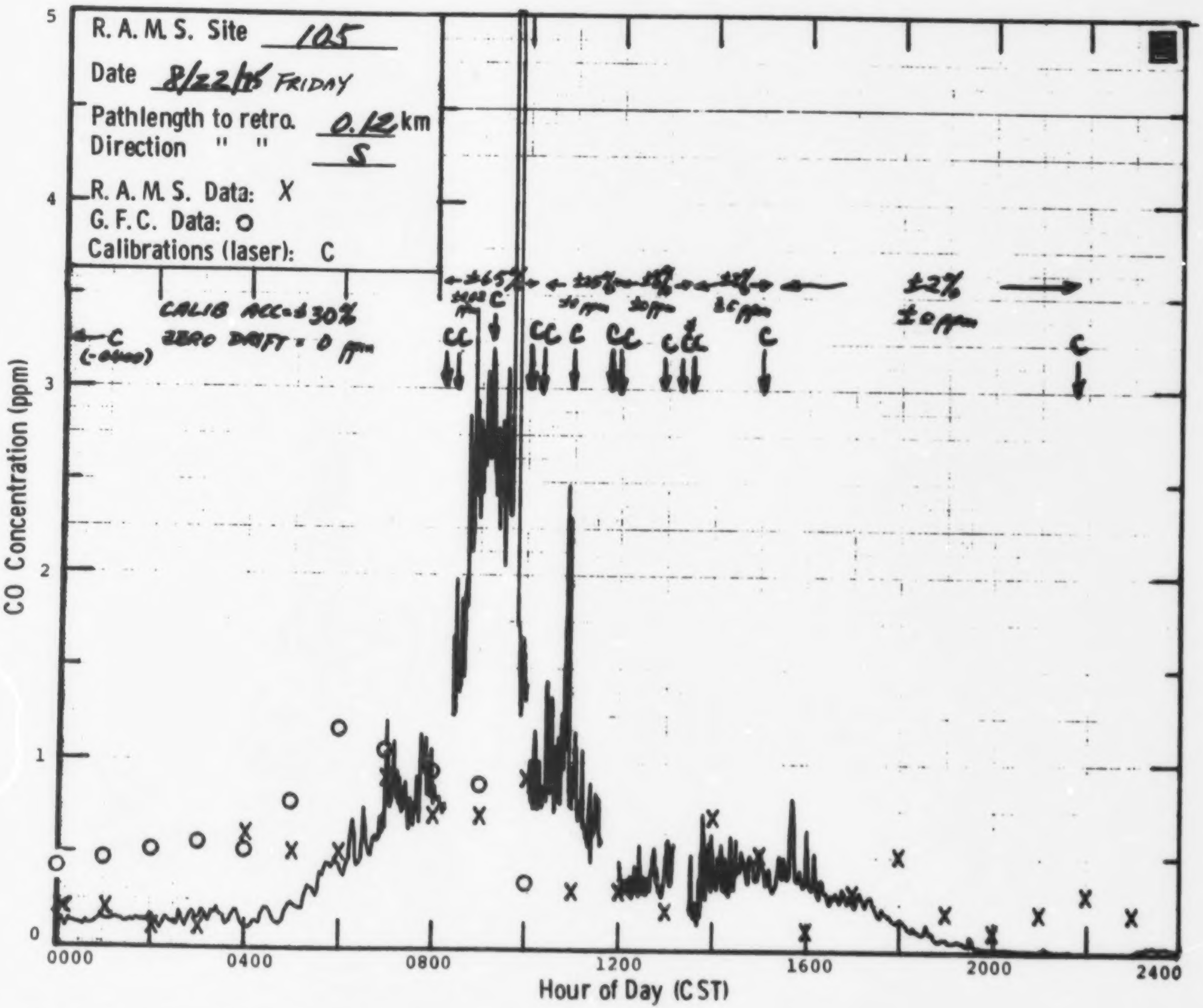
R. A. M. S. Site 105
Date 8/15/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. Data: O
Calibrations (laser): C
CALIB ACC = ±12%
ZERO DRIFT ≈±0.14 ppm
±2%
±0.04 ppm
C
(0230)
C
(2400)
5
4
3
2
1
0
CO Concentration (ppm)
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)

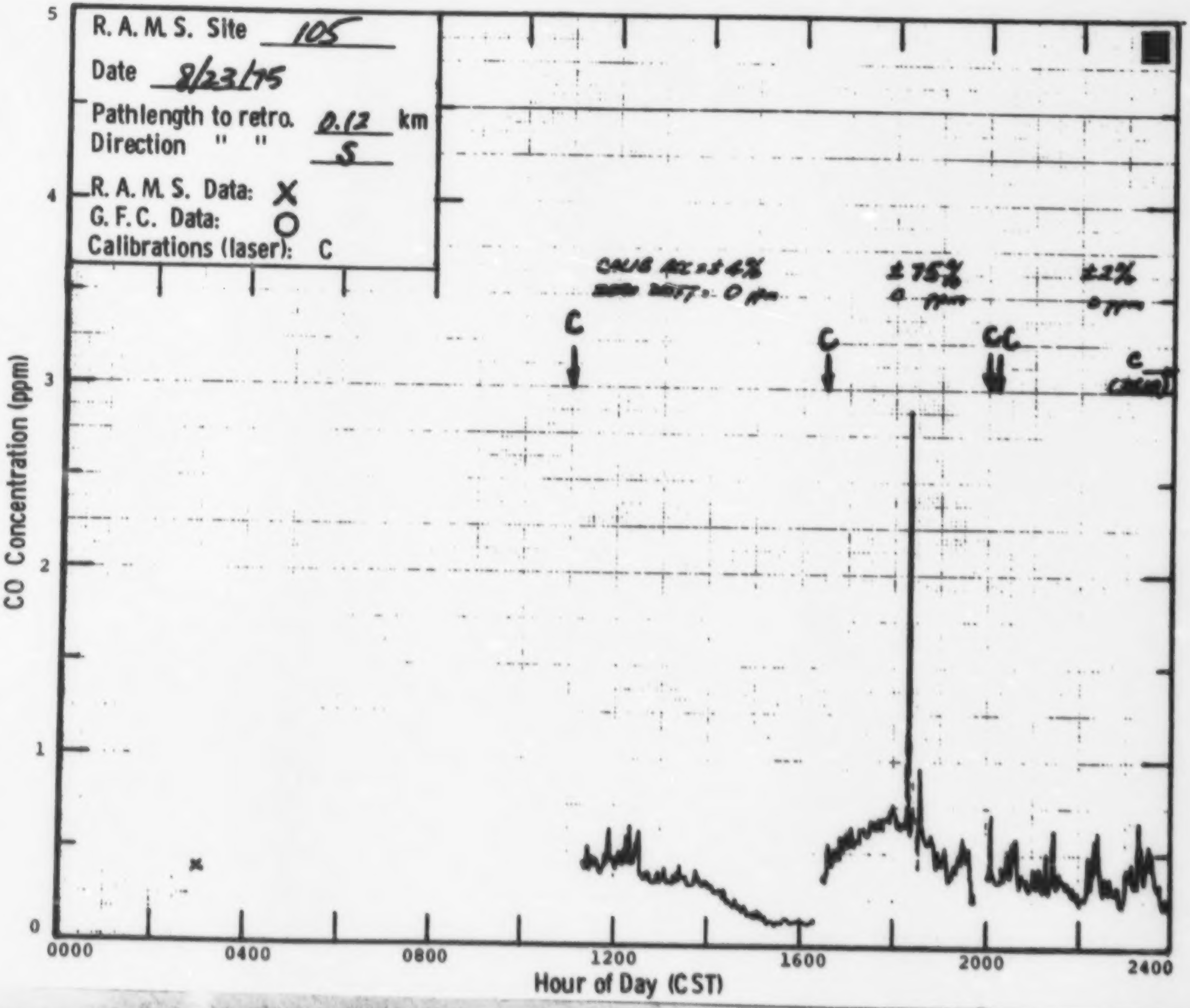

R. A. M. S. Site 105
Date 8/16/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: ○
Calibrations (laser): C
CALIB ACC = ±5%
ZERO DRIFT = ±0.25 ppm
C
(-0.2 ppm)
C
C C
±11%
± 0 ppm
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 105
Date 8/17/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
CALIB ACC = ±6%
ZERO DRIFT = 0ppm
C
(~0100)
C
C
±8%
±0 ppm
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)

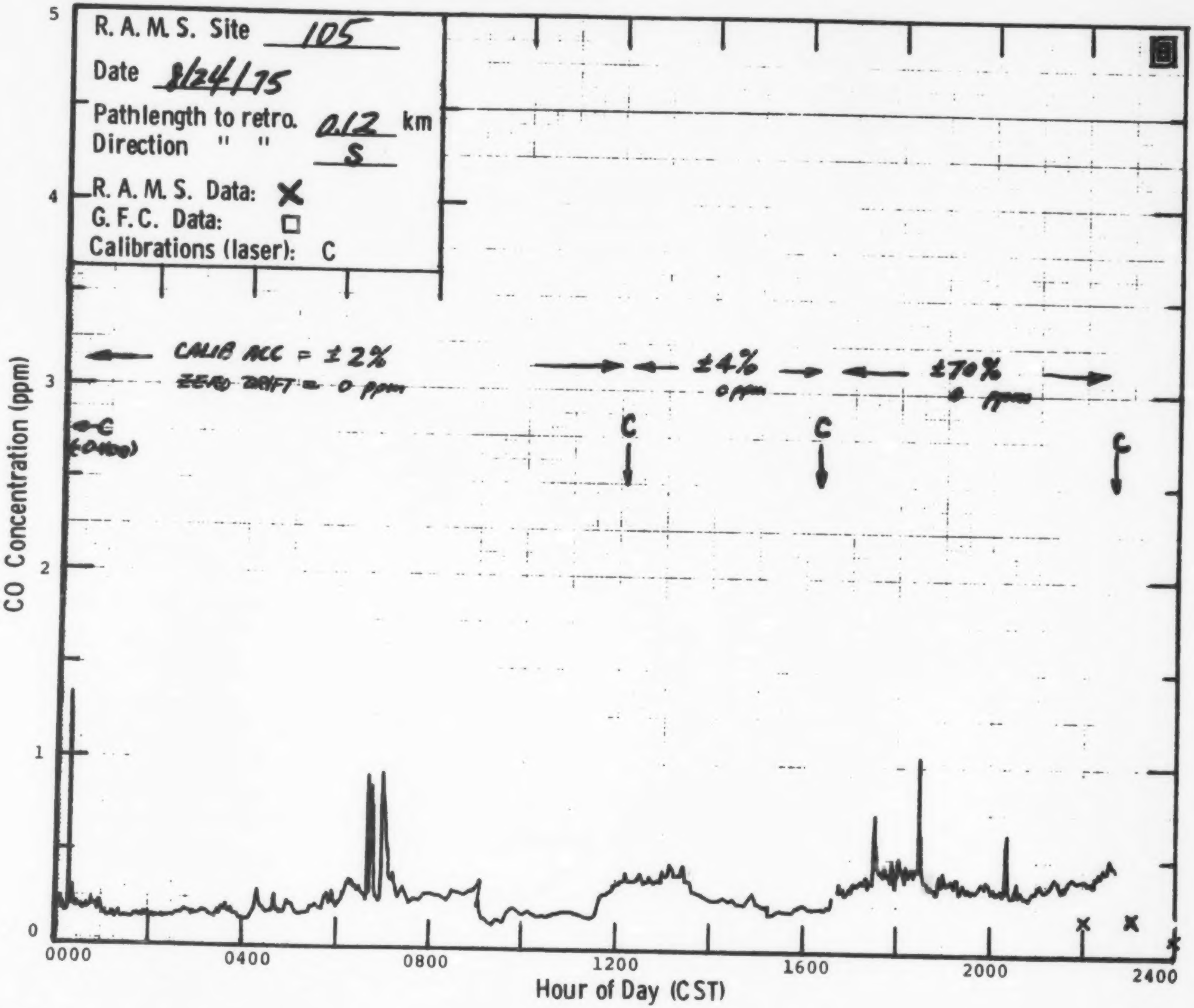
R. A. M. S. Site 105
Date 8/20/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: ×
G. F. C. Data: ○
Calibrations (laser): C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400
C
Q & C
C
CALIB. ACC ± 6%
ZERO DRIFT ±0.003 ppm


RAM SITE = 105
DATE : 8/21/75
PATH LENGTH : 0.65 Km N
0.12 Km S
RAMS DATA : X , CALIB : C
QFC DATA : O
0.65 Km
CALIB ACC = ±30%
ZERO DRIFT = ±.10 ppm
←C (~0300)
±3%
±.10 ppm
±16%
±0.03 ppm
C
C*
C→ (2300)
CO CONCENTRATION (PPM)
HOUR OF DAY (CST)
0
2
4
6
8
10
12
14
16
18
20
22
24
2
4
6
8
10
12
14
16
18
20


R. A. M. S. Site 105
Date 8/22/75 FRIDAY
Pathlength to retro. 0.12 km
Direction " " S
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
CALIB ACC=±30%
ZERO DRIFT = 0 ppm
C (-0400)
±65%
C
CC
CC C
CC
C CC
C
±25%
±10 ppm
±5%
±0 ppm
±2%
±5 ppm
±2%
±0 ppm
C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400



R. A. M. S. Site 105
Date 8/23/75
Pathlength to retro. 0.12 km
Direction " " S
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C



R. A. M. S. Site 105

Date 8/24/75

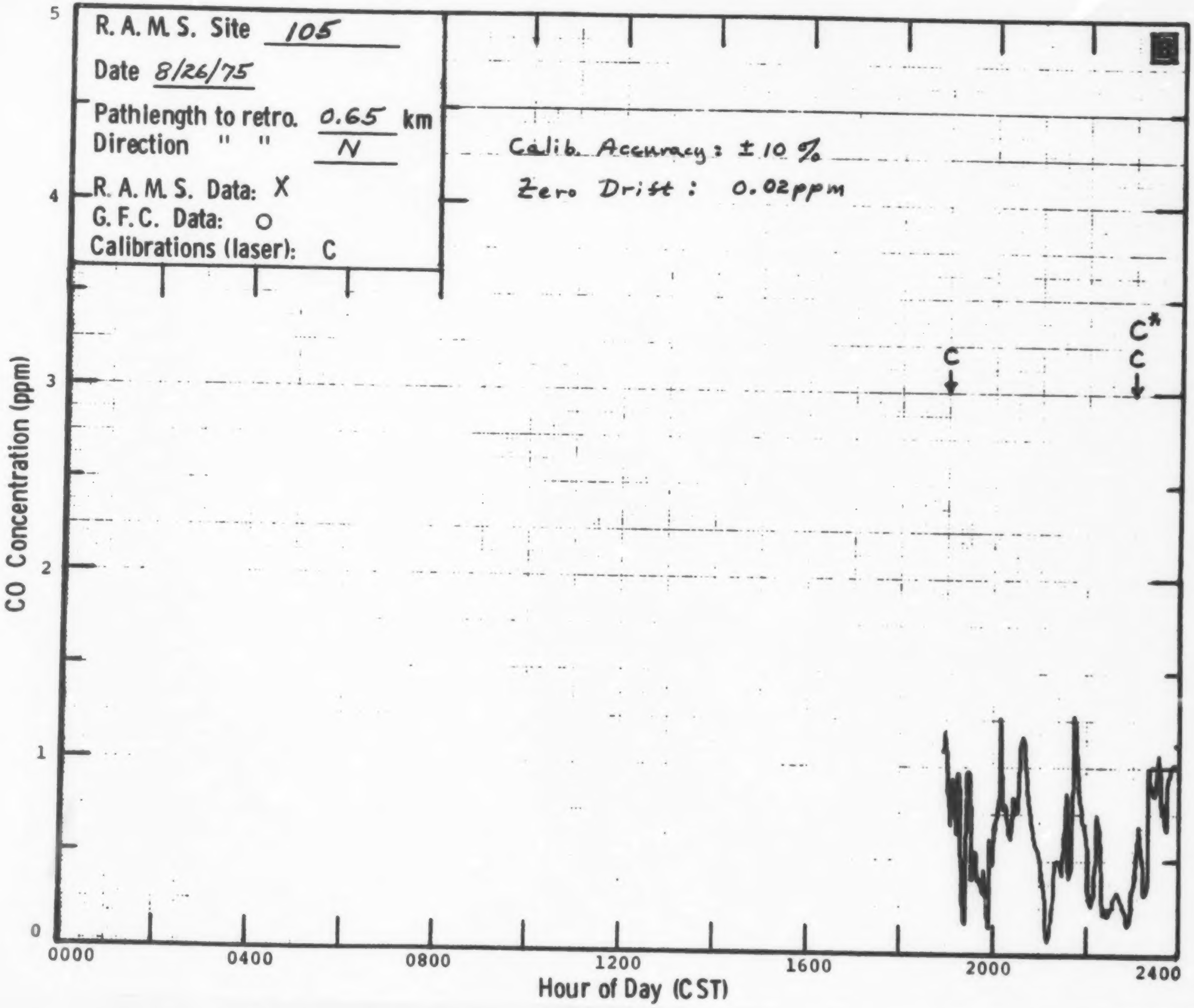
Pathlength to retro. 0.12 km

Direction " " S

R. A. M. S. Data: ☒

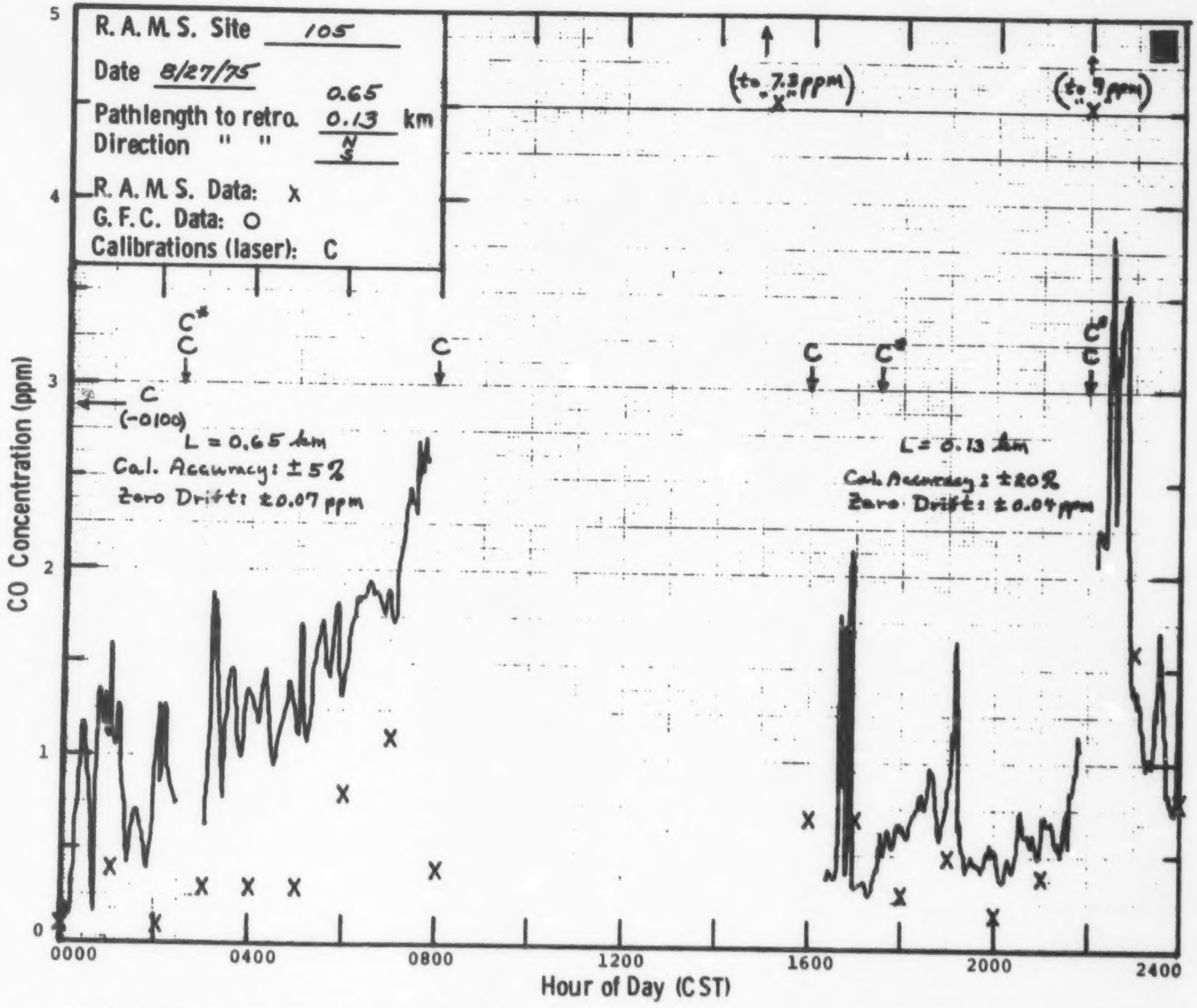
G. F. C. Data: ☐

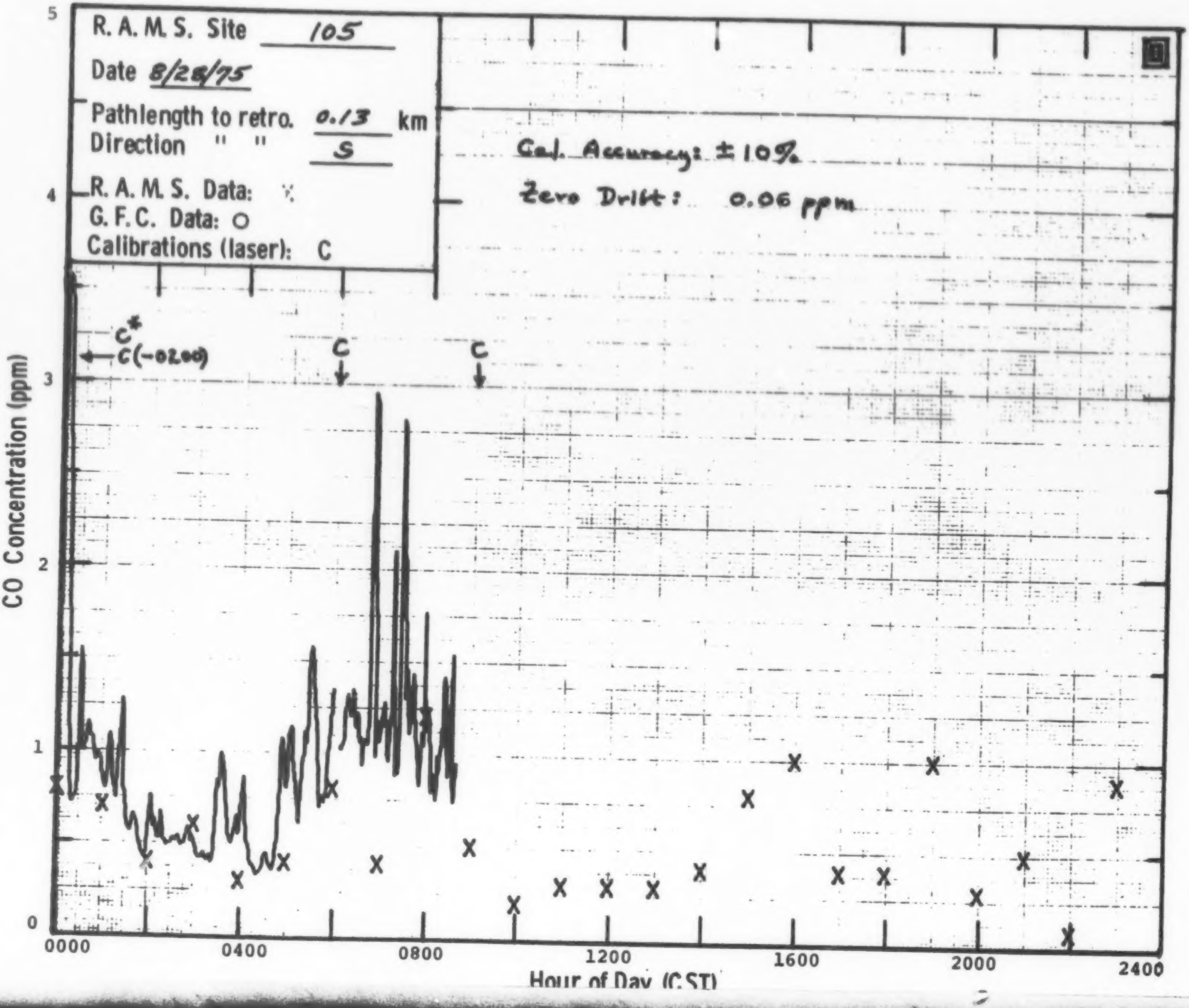
Calibrations (laser): C

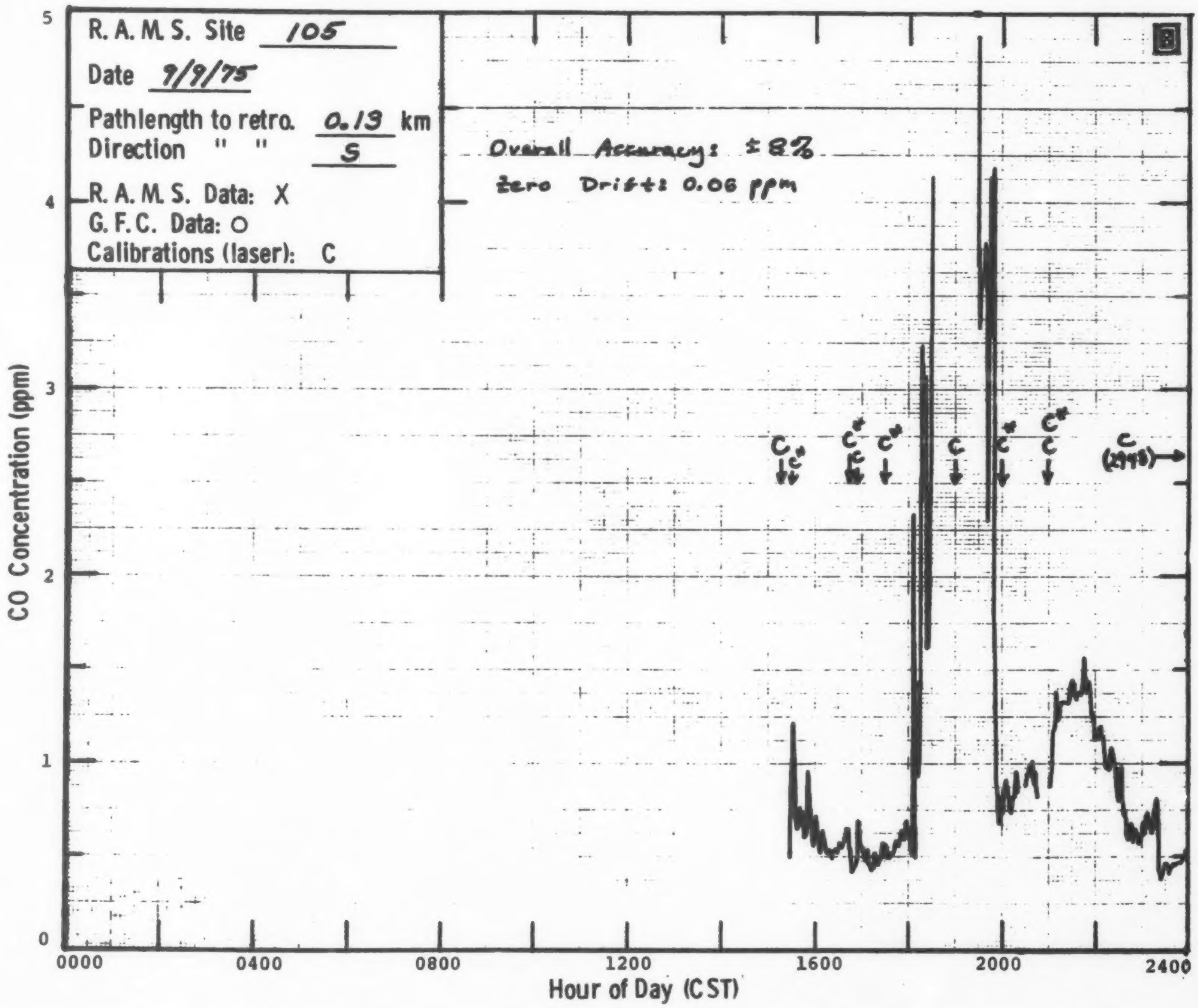


R. A. M. S. Site 105
Date 8/26/75
Pathlength to retro. 0.65 km
Direction " " N
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C

Calib. Accuracy: ± 10 %
Zero Drift: 0.02ppm


R. A. M. S. Site 105
Date 8/27/75
Pathlength to retro. 0.65 0.13 km
Direction " " N S
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
C* C
C
C (-0100)
L = 0.65 km
Cal. Accuracy: ±5%
Zero Drift: ±0.07 ppm
C
C*
C* C
(to 7.3 ppm) "X"
(to 9 ppm) "X"
L = 0.13 km
Cal. Accuracy: ±20%
Zero Drift: ±0.04 ppm
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 105
Date 8/28/75
Pathlength to retro. 0.13 km
Direction " " S
R. A. M. S. Data: X
G. F. C. Data: O
Calibrations (laser): C
Cal. Accuracy: ± 10%
Zero Drift: 0.06 ppm
C*
C(-0200)
C
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 105

Date 9/9/75

Pathlength to retro. 0.13 km

Direction " " S

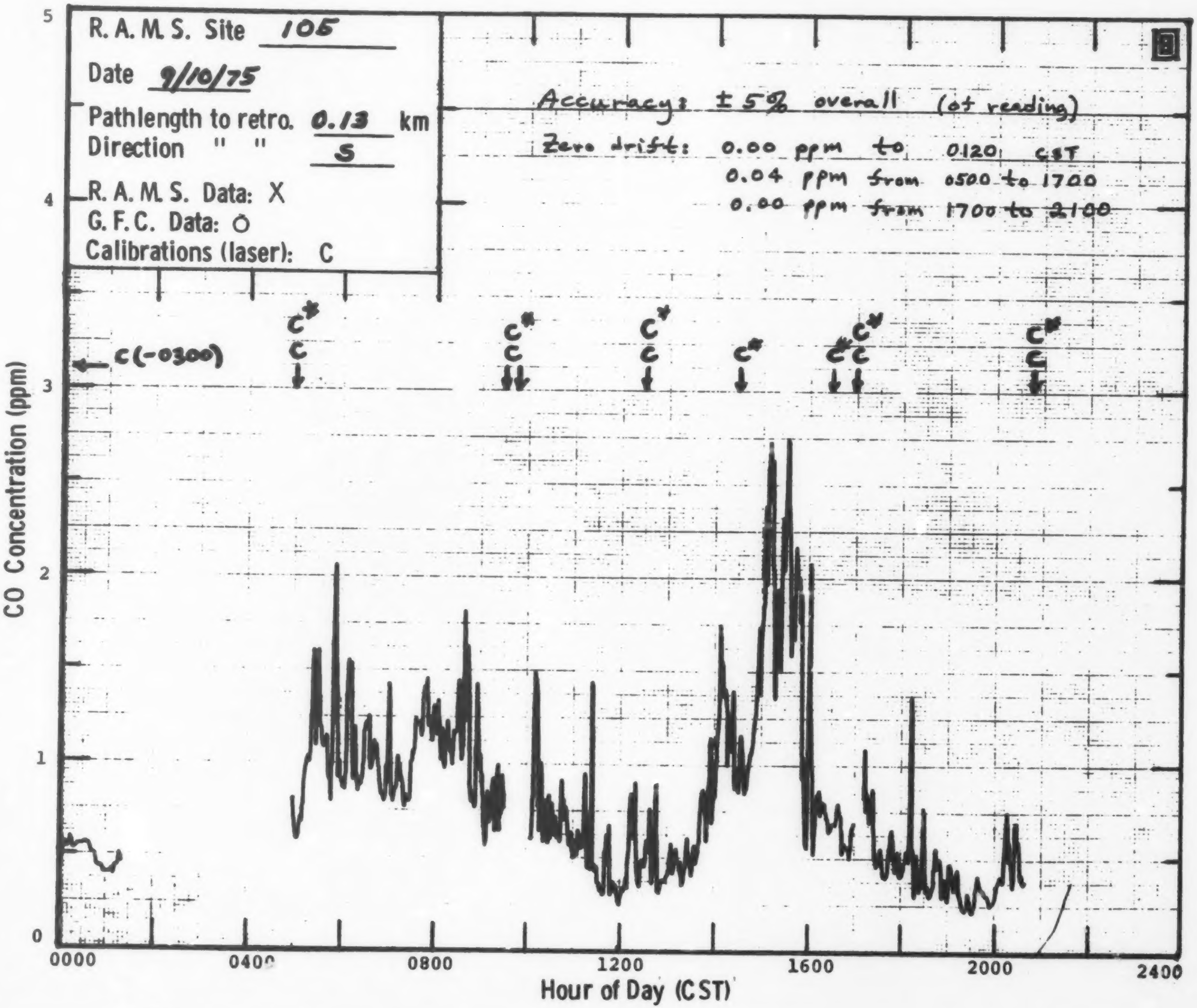
R. A. M. S. Data: X

G. F. C. Data: O

Calibrations (laser): C

Overall Accuracy: ± 8%

Zero Drift: 0.06 ppm



R. A. M. S. Site 105

Date 9/10/75

Pathlength to retro. 0.13 km

Direction " " S

R. A. M. S. Data: X

G. F. C. Data: O

Calibrations (laser): C

Accuracy: ± 5% overall (of reading)

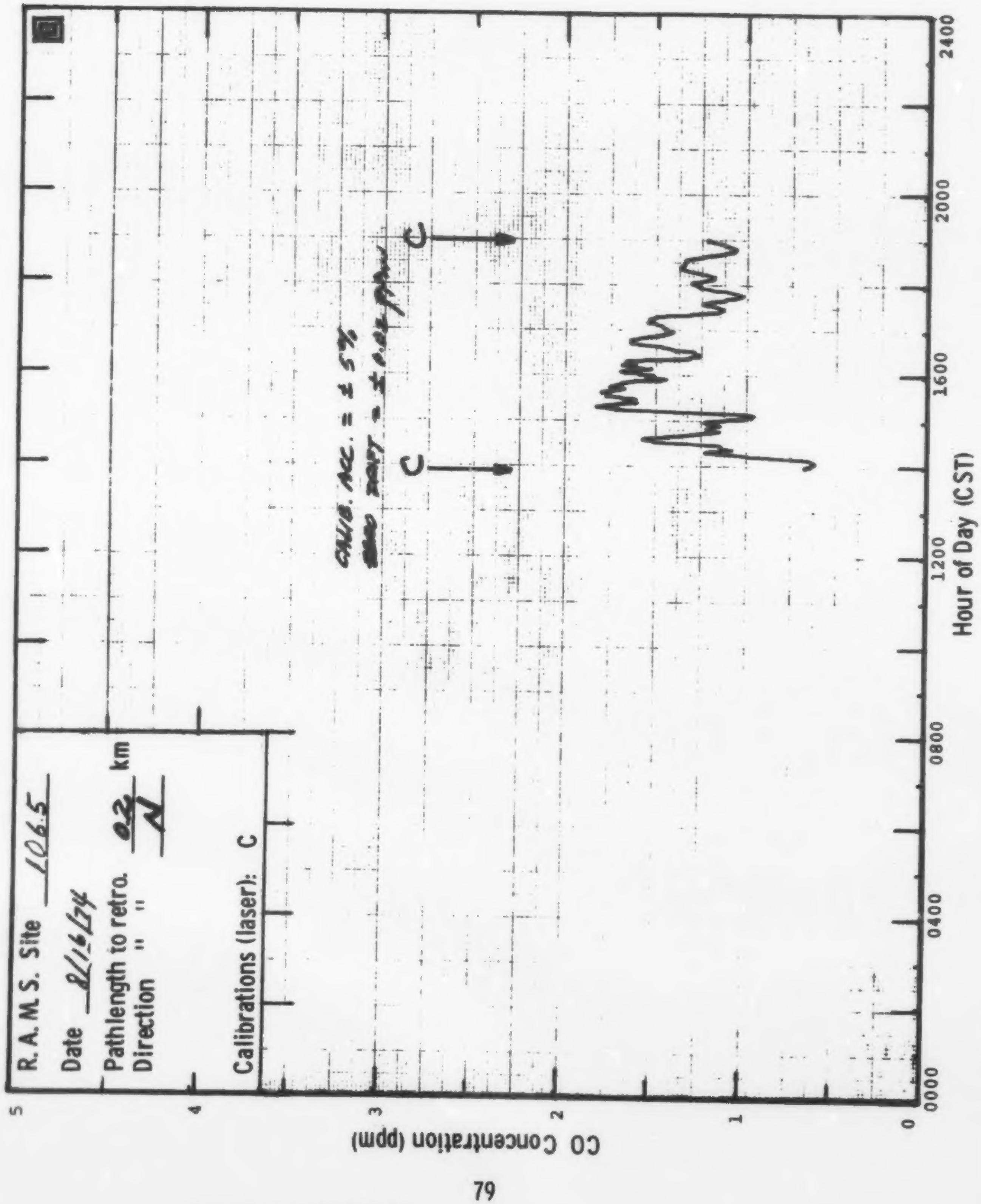
Zero drift: 0.00 ppm to 0120 CST

0.04 ppm from 0500 to 1700

0.00 ppm from 1700 to 2100

APPENDIX B

1974 RAPS Measurement Data



R. A. M. S. Site 106.5

Date 8/16/74

Pathlength to retro. 0.2 km

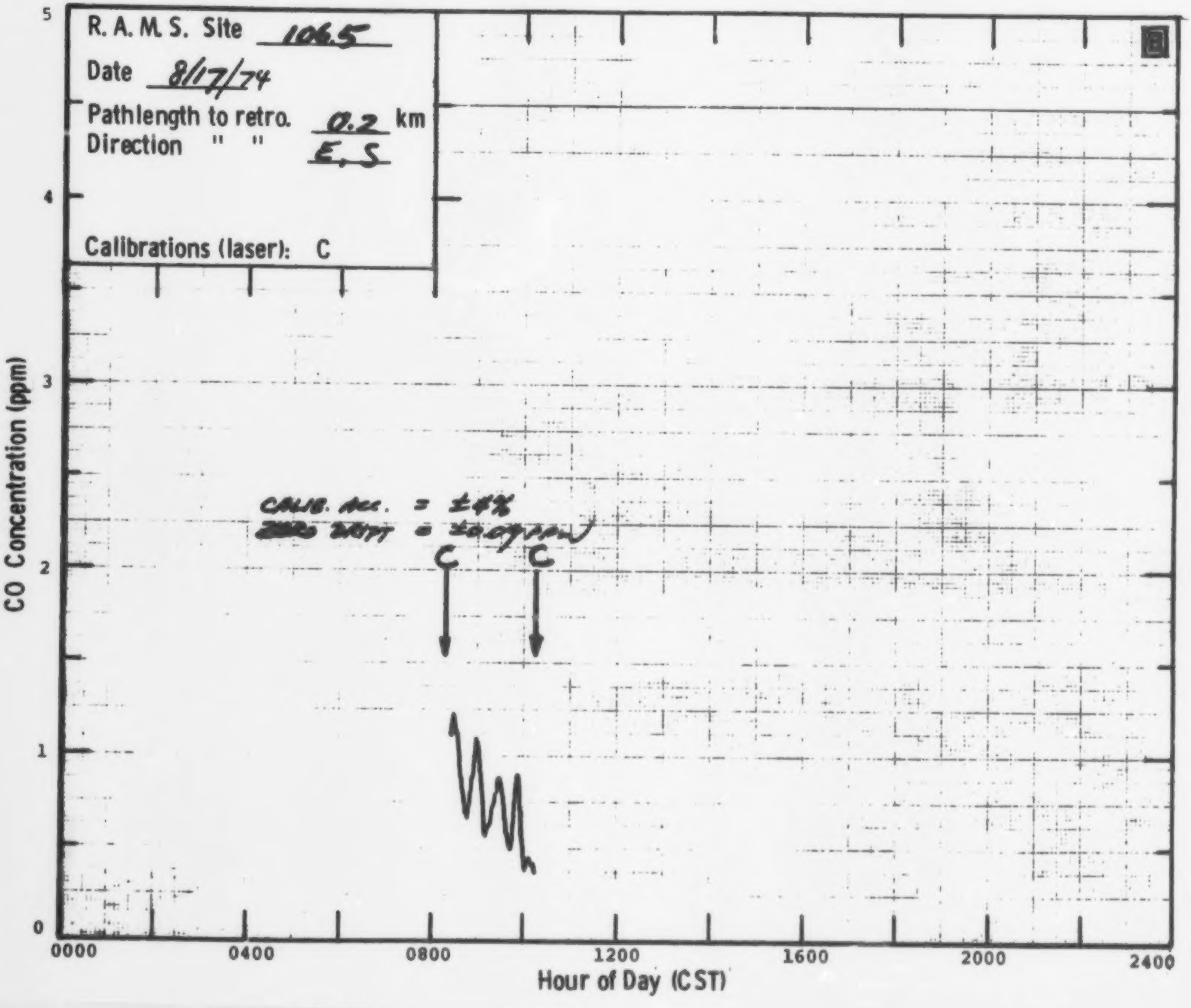
Direction N

Calibrations (laser): C

CALIB. ACC. = ± 5%

ZERO DRIFT = ± 0.02 ppm

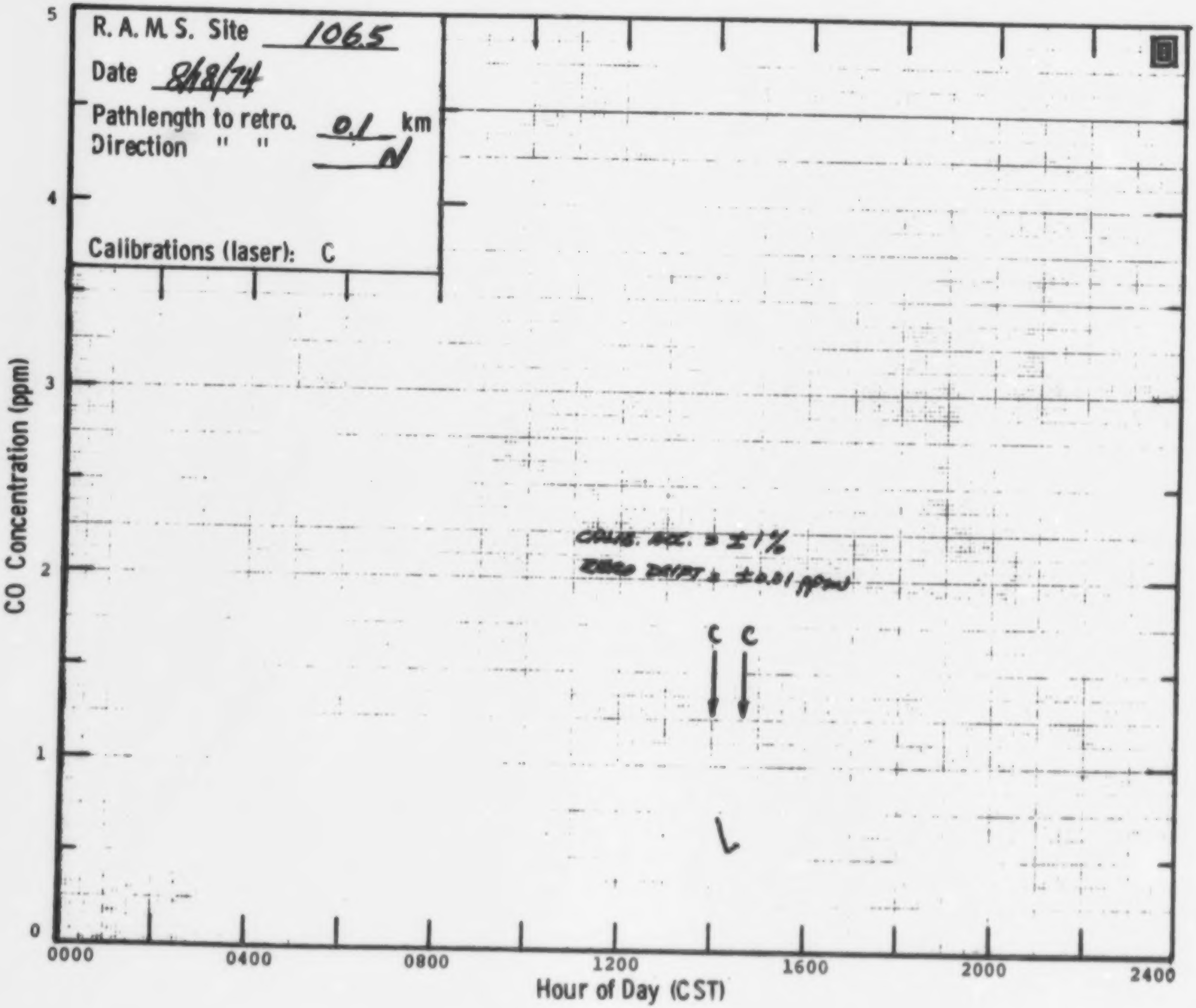
Preceding page blank



R. A. M. S. Site 106.5
Date 8/17/74
Pathlength to retro. 0.2 km
Direction " " E, S

Calibrations (laser): C

CALIB. ACC. = ±4%
ZERO DRIFT = ±0.09 PPM


R. A. M. S. Site 106.5

Date 8/8/74

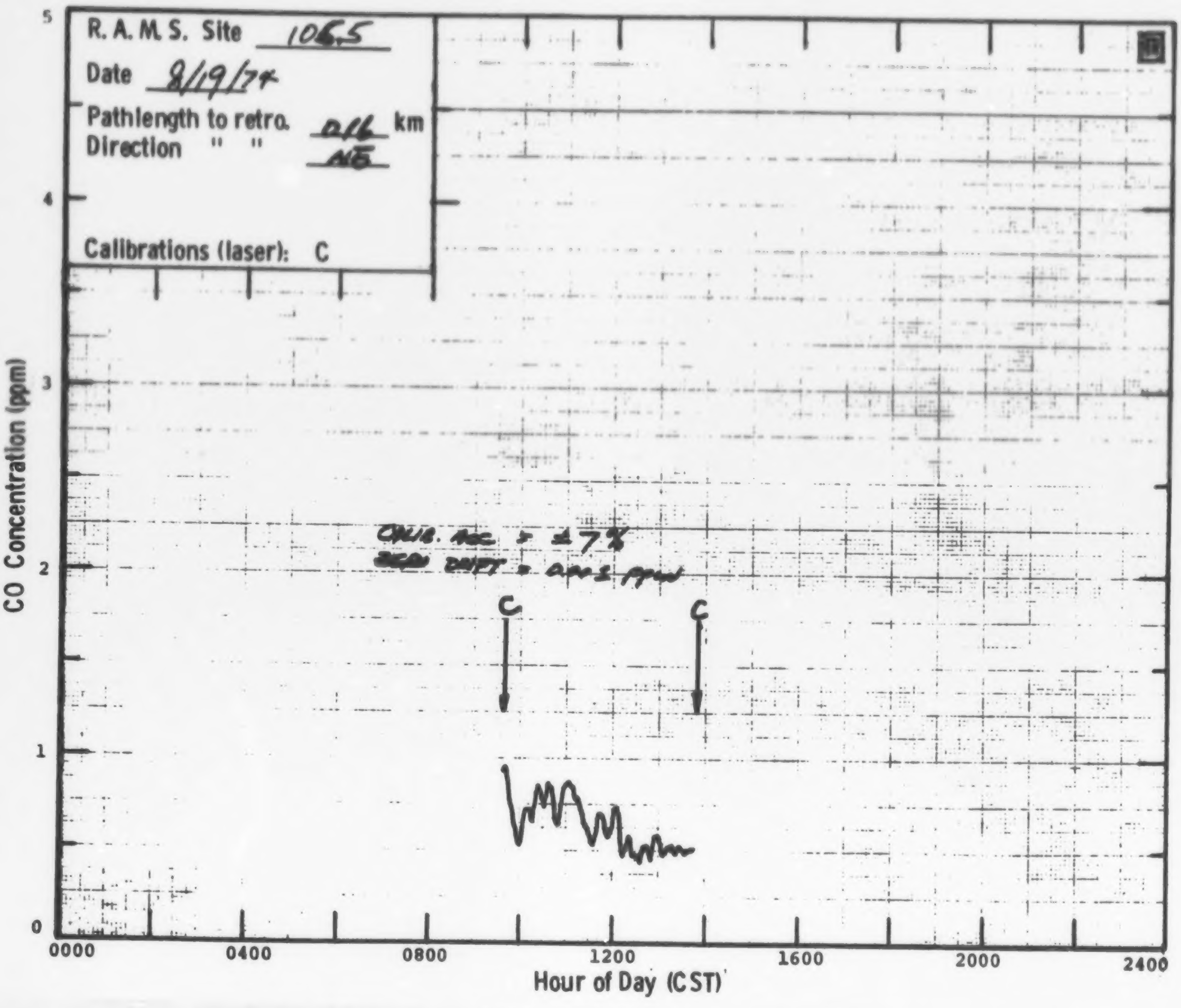
Pathlength to retro. 0.1 km

Direction " " N

Calibrations (laser): C

CALIB. ACC. ≈ ±1%

ZERO DRIFT ≈ ±0.01 ppm



R. A. M. S. Site 106.5

Date 8/19/74

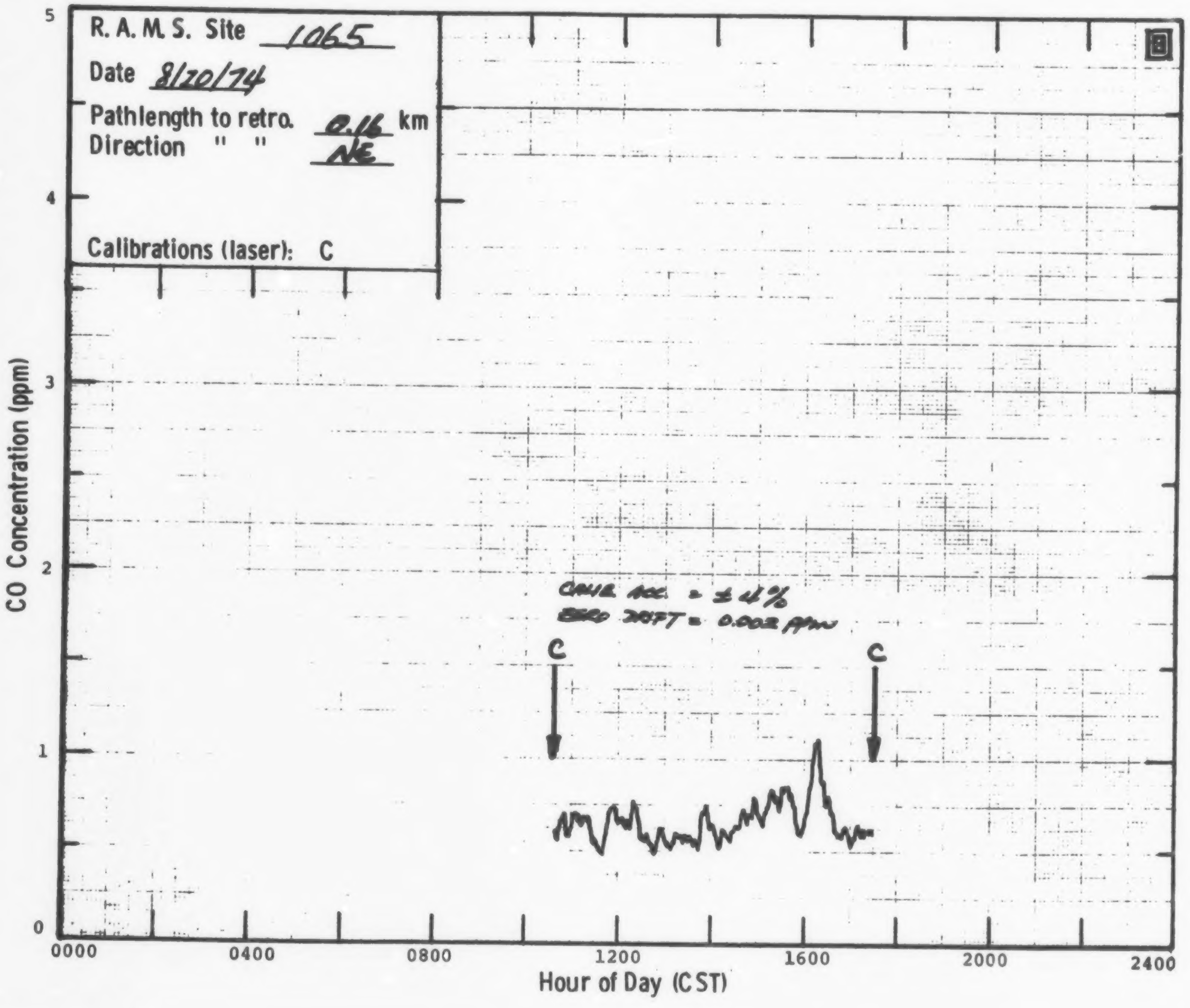
Pathlength to retro. 0.16 km

Direction " " NE

Calibrations (laser): C

CALIB. ACC = ±7%

ZERO DRIFT = 0.05 ppm



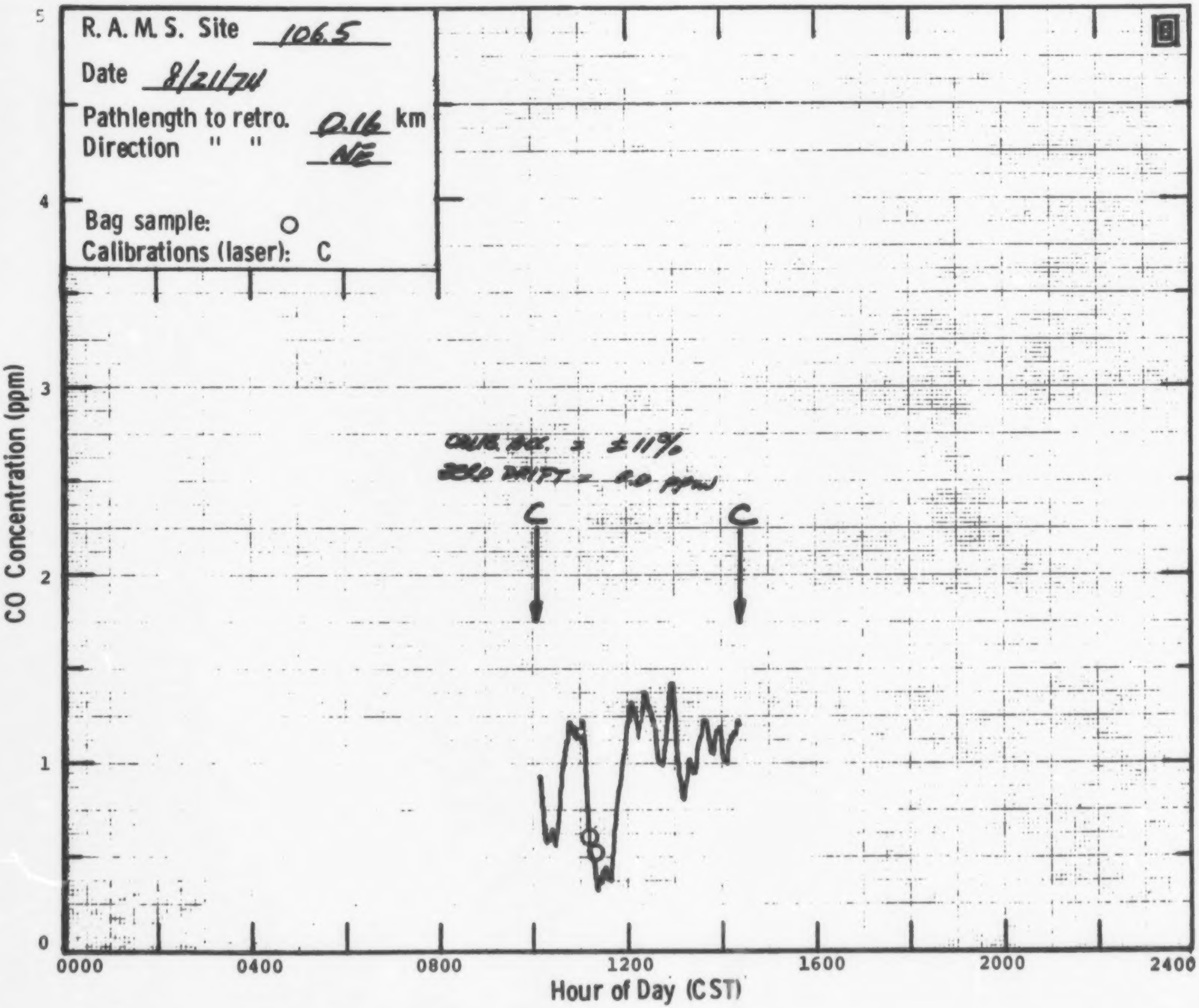
R. A. M. S. Site 106.5

Date 8/20/74

Pathlength to retro. 0.16 km

Direction " " NE

Calibrations (laser): C



R. A. M. S. Site 106.5

Date 8/21/74

Pathlength to retro. 0.16 km

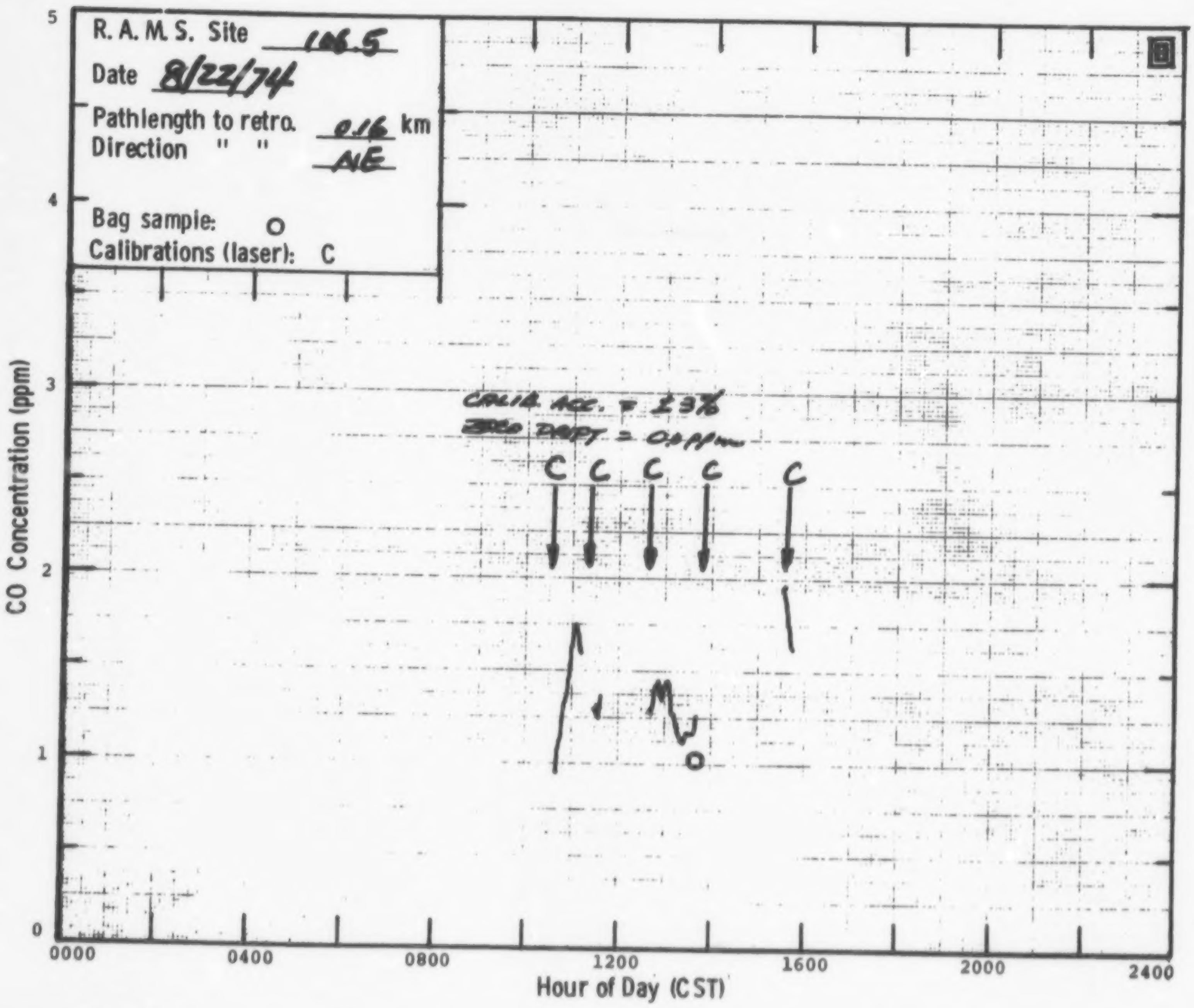
Direction " " NE

Bag sample: ○

Calibrations (laser): C

CALIB. ACC. = ±11%

ZERO DRIFT = 0.0 ppm



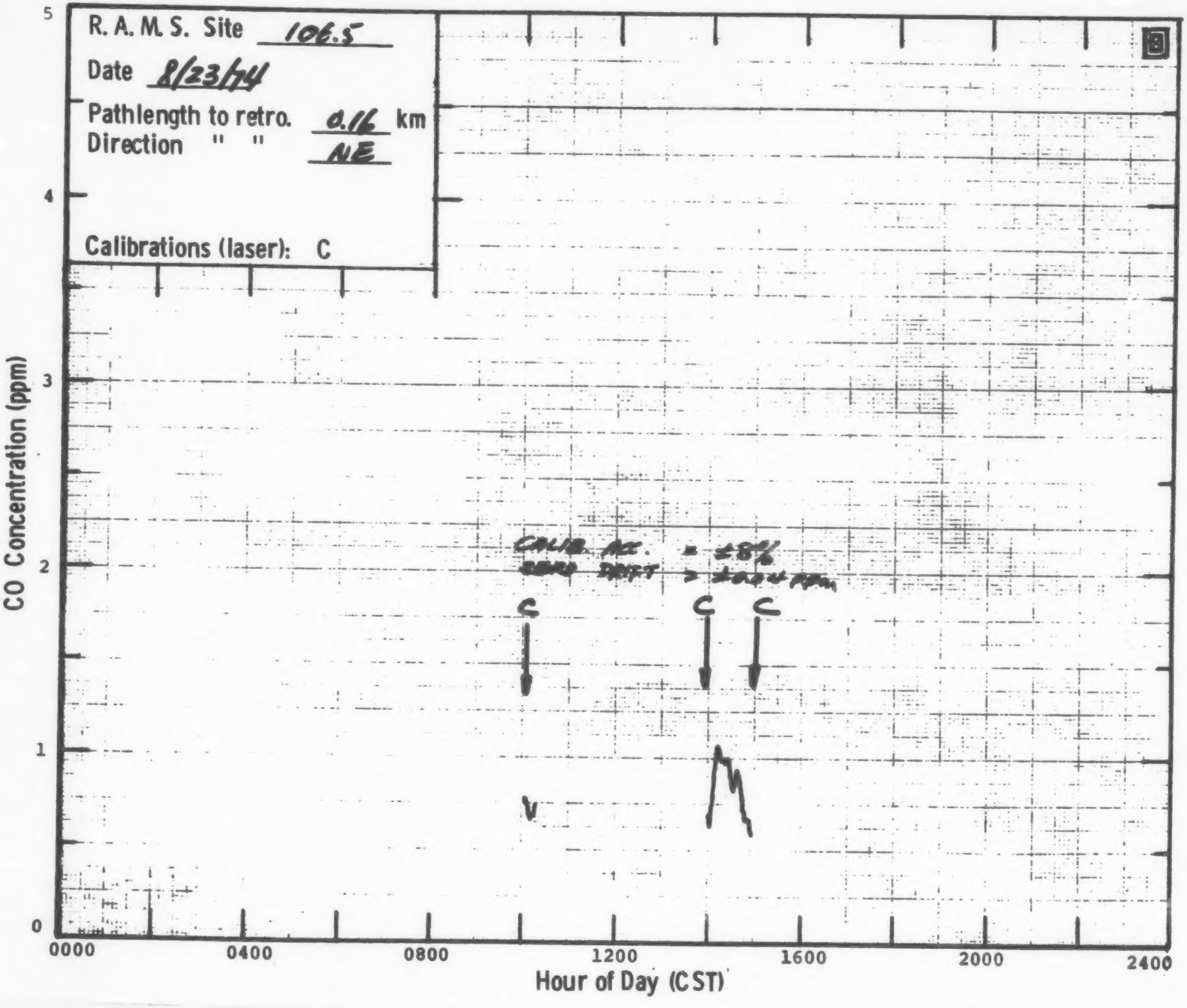
R. A. M. S. Site 106.5
Date 8/22/74
Pathlength to retro. 0.16 km
Direction " " NE

Bag sample: O
Calibrations (laser): C

CALIB. ACC. = ± 3%
ZERO DRIFT = 0.0 ppm

R. A. M. S. Site 106.5
Date 8/23/74
Pathlength to retro. 0.16 km
Direction " " NE

Calibrations (laser): C



CALIB. ACC. = ±8%
ZERO DRIFT > ±0.04 PPM

R. A. M. S. Site 106.5

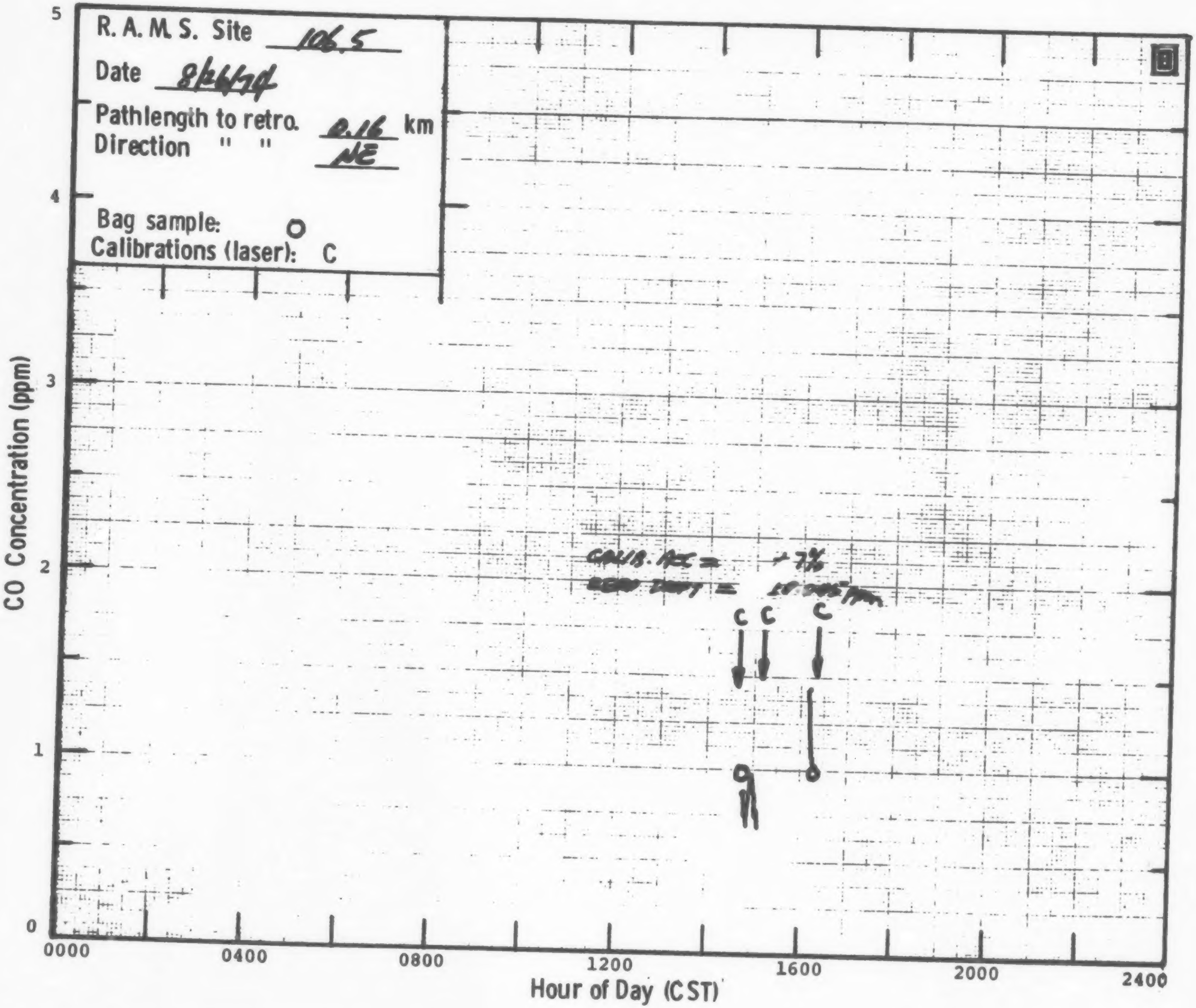
Date 8/26/74

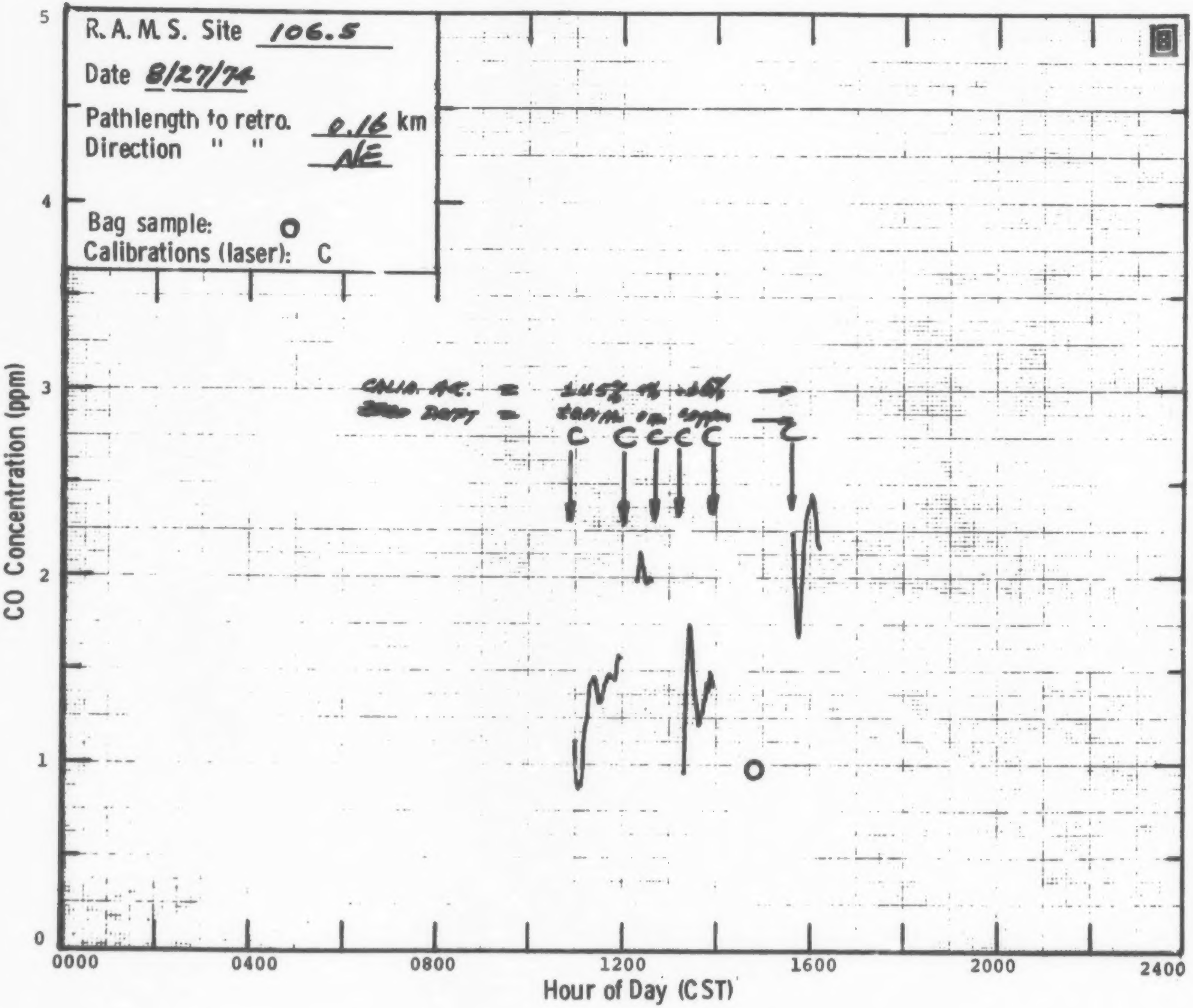
Pathlength to retro. 0.16 km

Direction " " NE

Bag sample: ○

Calibrations (laser): C





R. A. M. S. Site 106.5

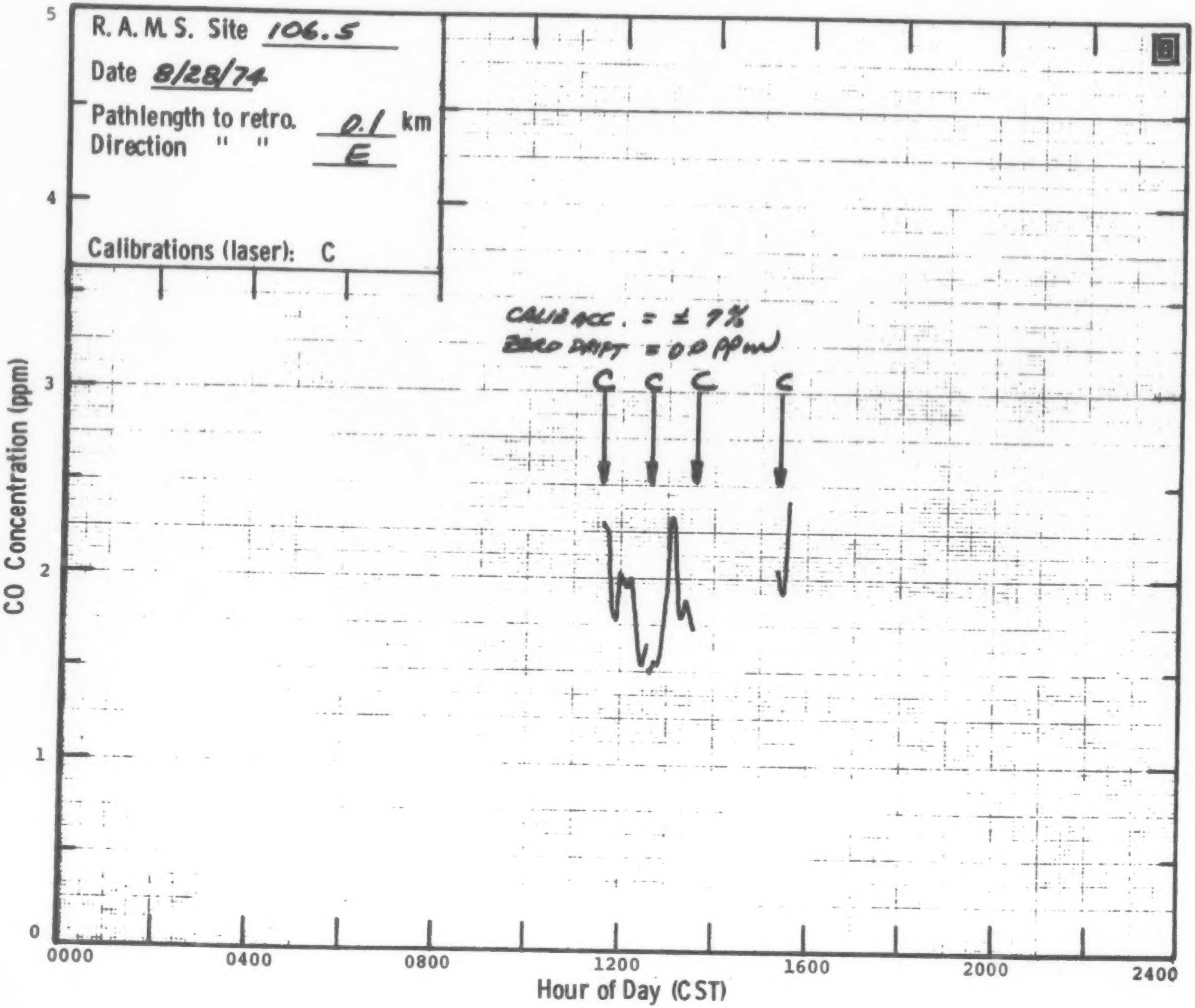
Date 8/27/74

Pathlength to retro. 0.16 km

Direction " " NE

Bag sample: O

Calibrations (laser): C



R. A. M. S. Site 106.5

Date 8/28/74

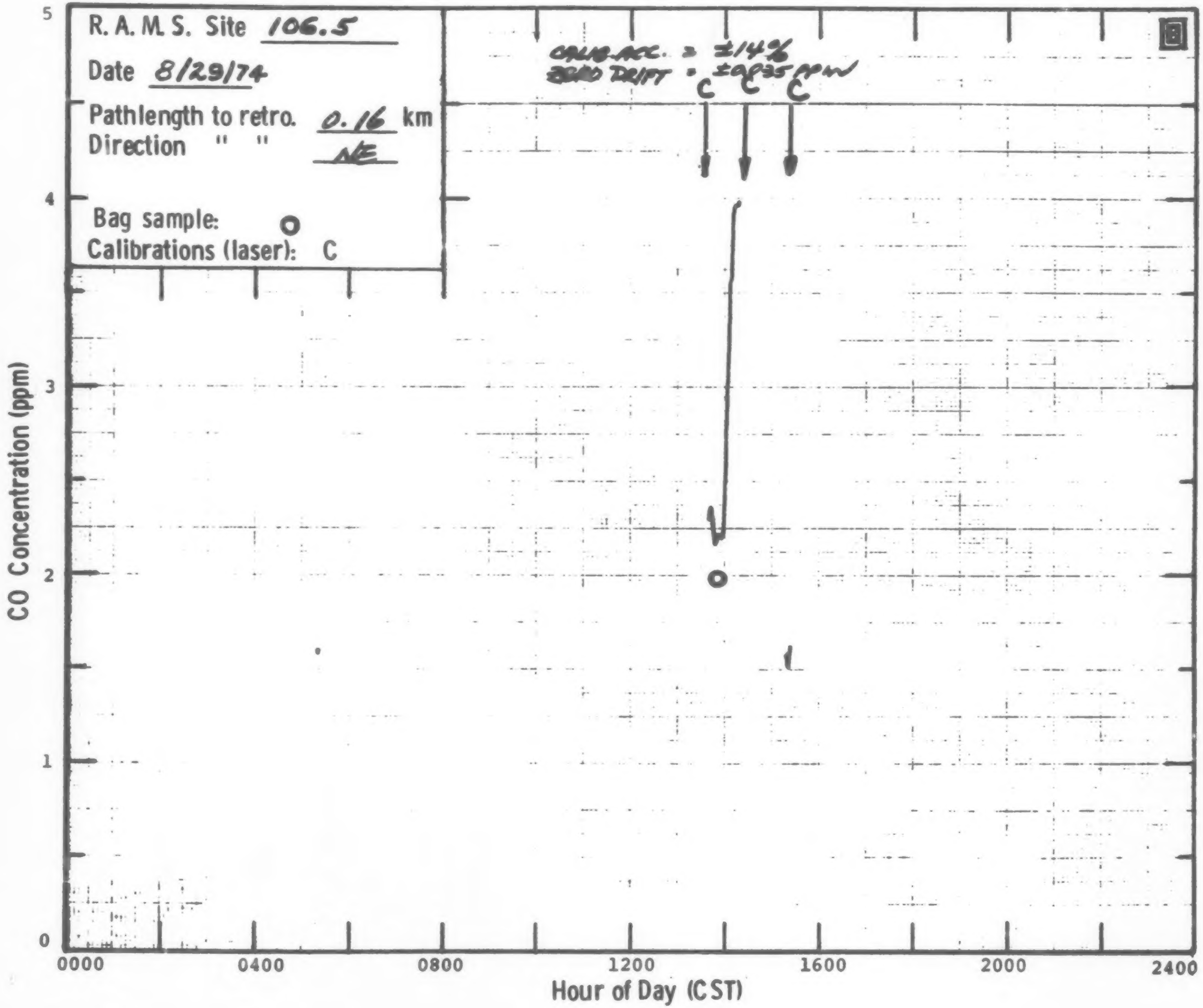
Pathlength to retro. 0.1 km

Direction " " E

Calibrations (laser): C

CALIB ACC. = ± 7%

ZERO DRIFT = 0.0 ppm



R. A. M. S. Site 106.5

Date 8/29/74

Pathlength to retro. 0.16 km

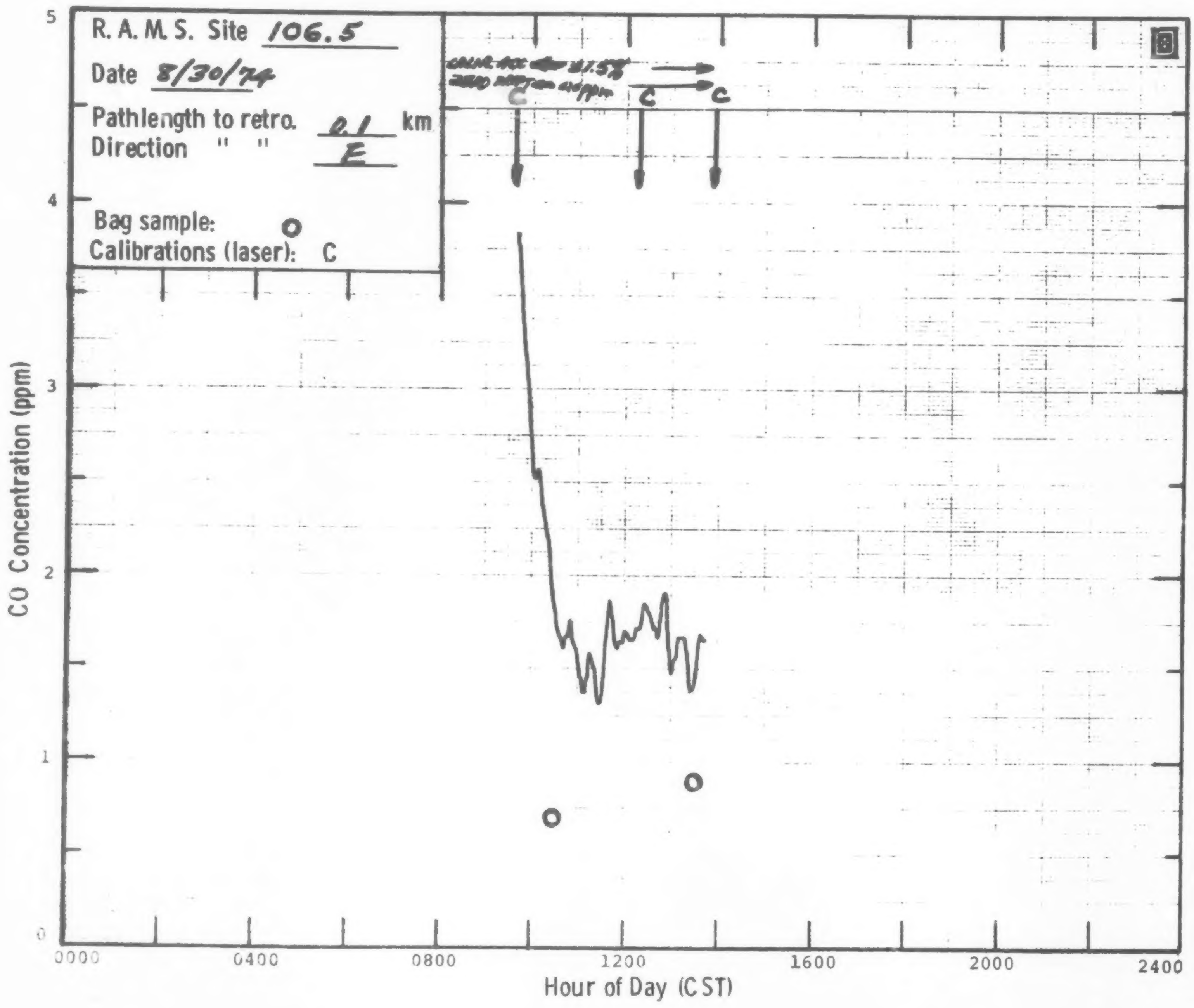
Direction " " NE

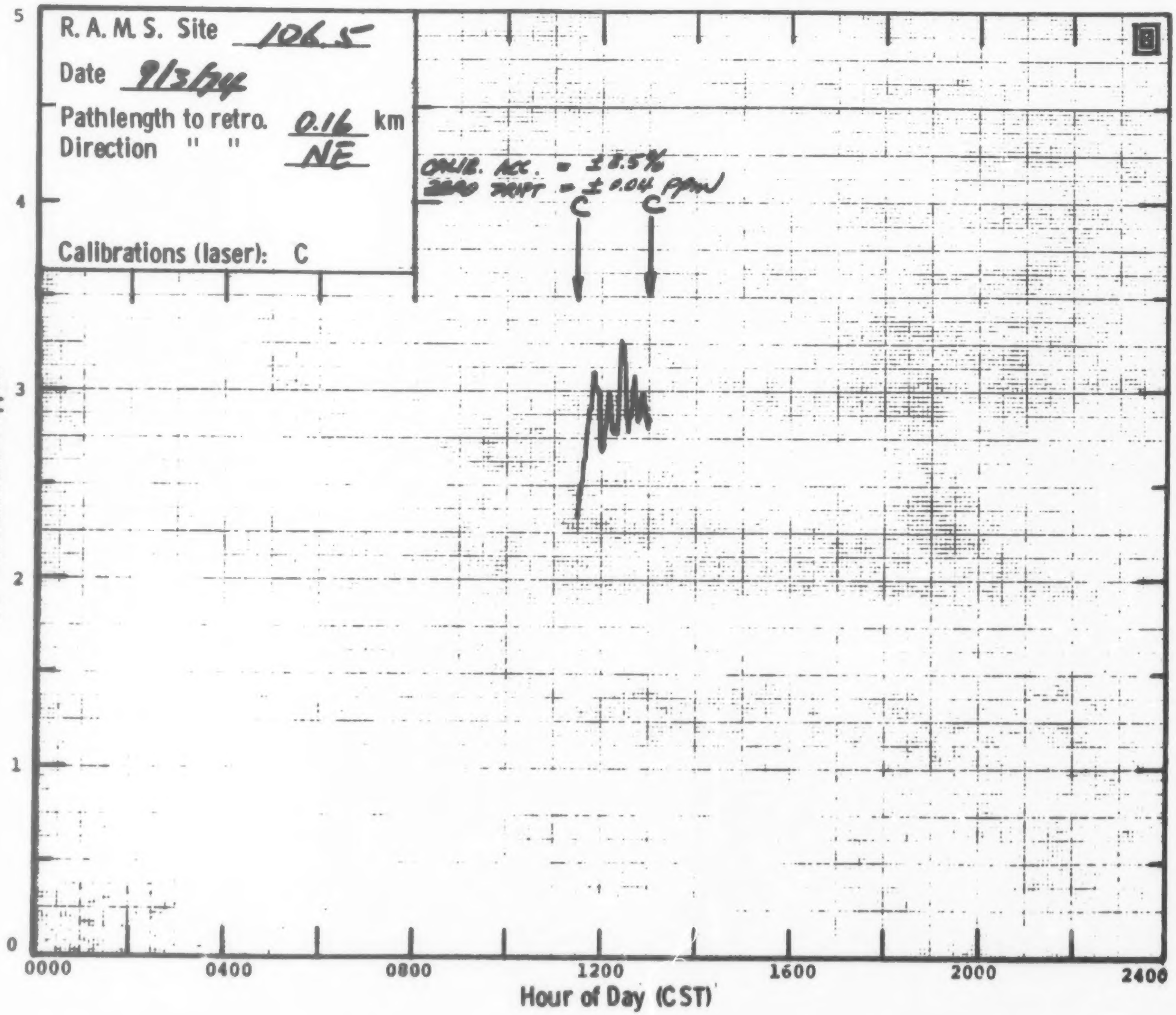
Bag sample: o

Calibrations (laser): C

CALIB. ACC. = ±14%

ZERO DRIFT = ±0.035 ppm


R. A. M. S. Site 106.5
Date 8/30/74
Pathlength to retro. 0.1 km
Direction " " E
Bag sample: O
Calibrations (laser): C
21.5%
ppm
C
C
C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)



R. A. M. S. Site 106.5

Date 9/13/74

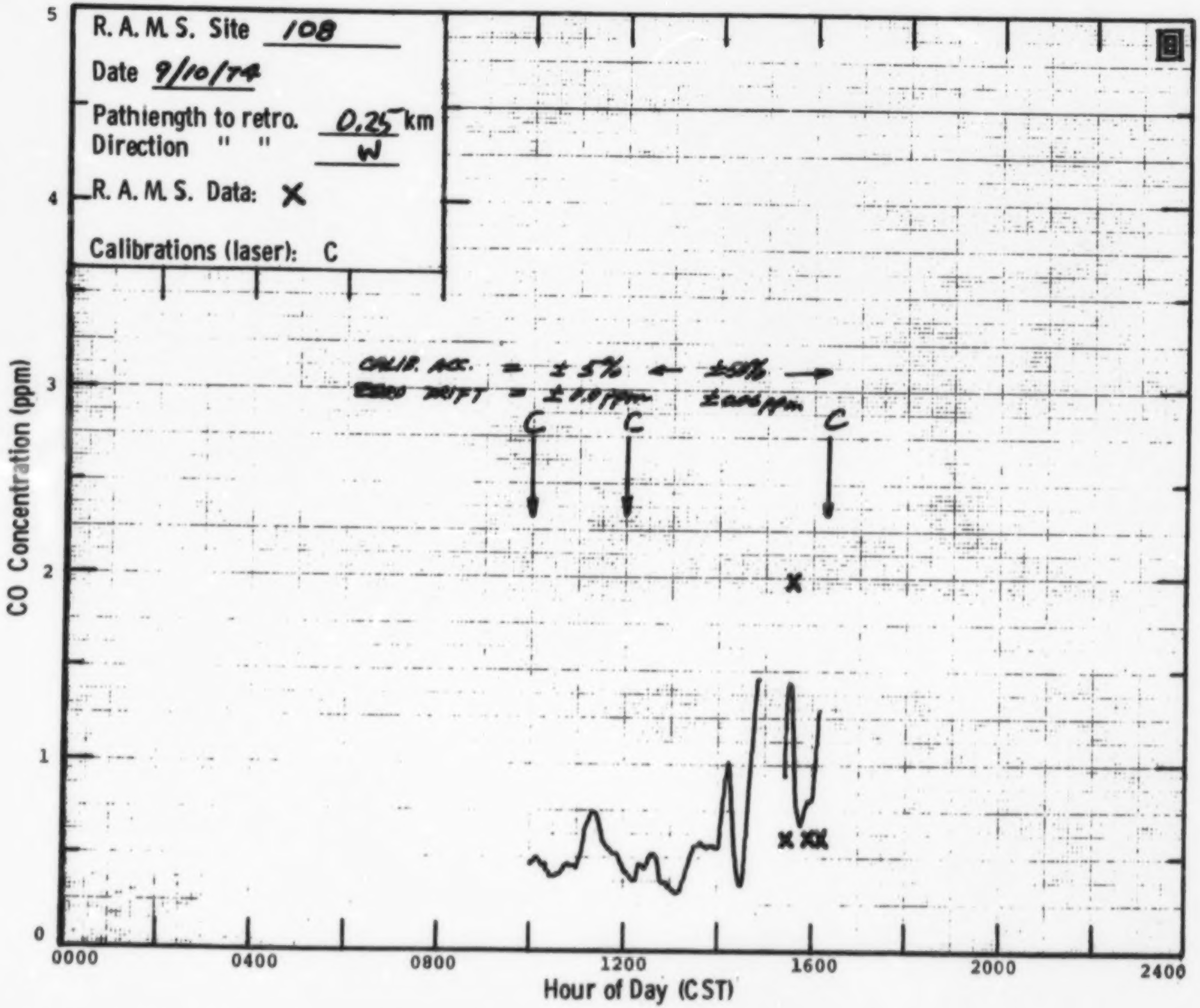
Pathlength to retro. 0.16 km

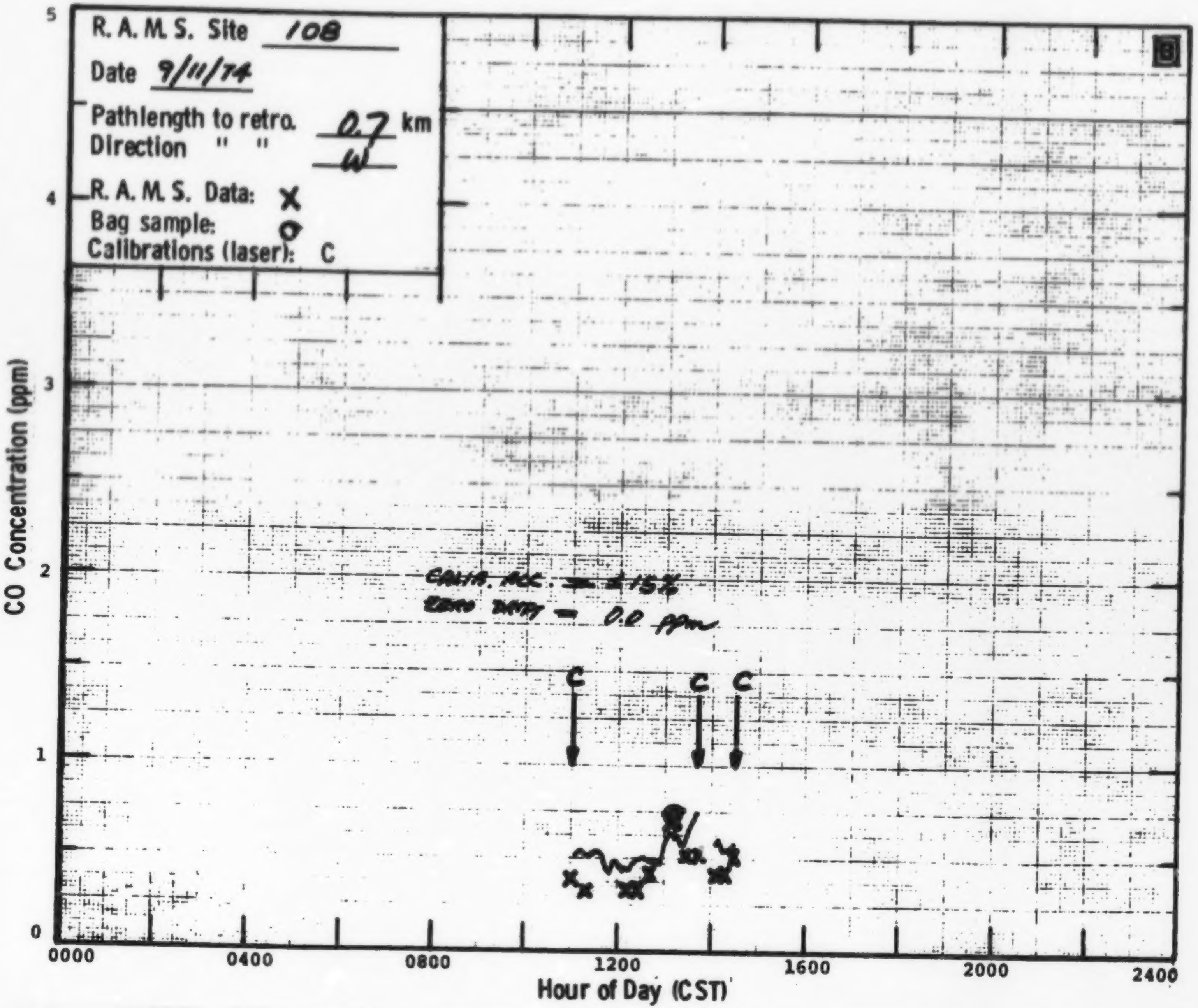
Direction " " NE

Calibrations (laser): C

CALIB. ACC. = ± 8.5%

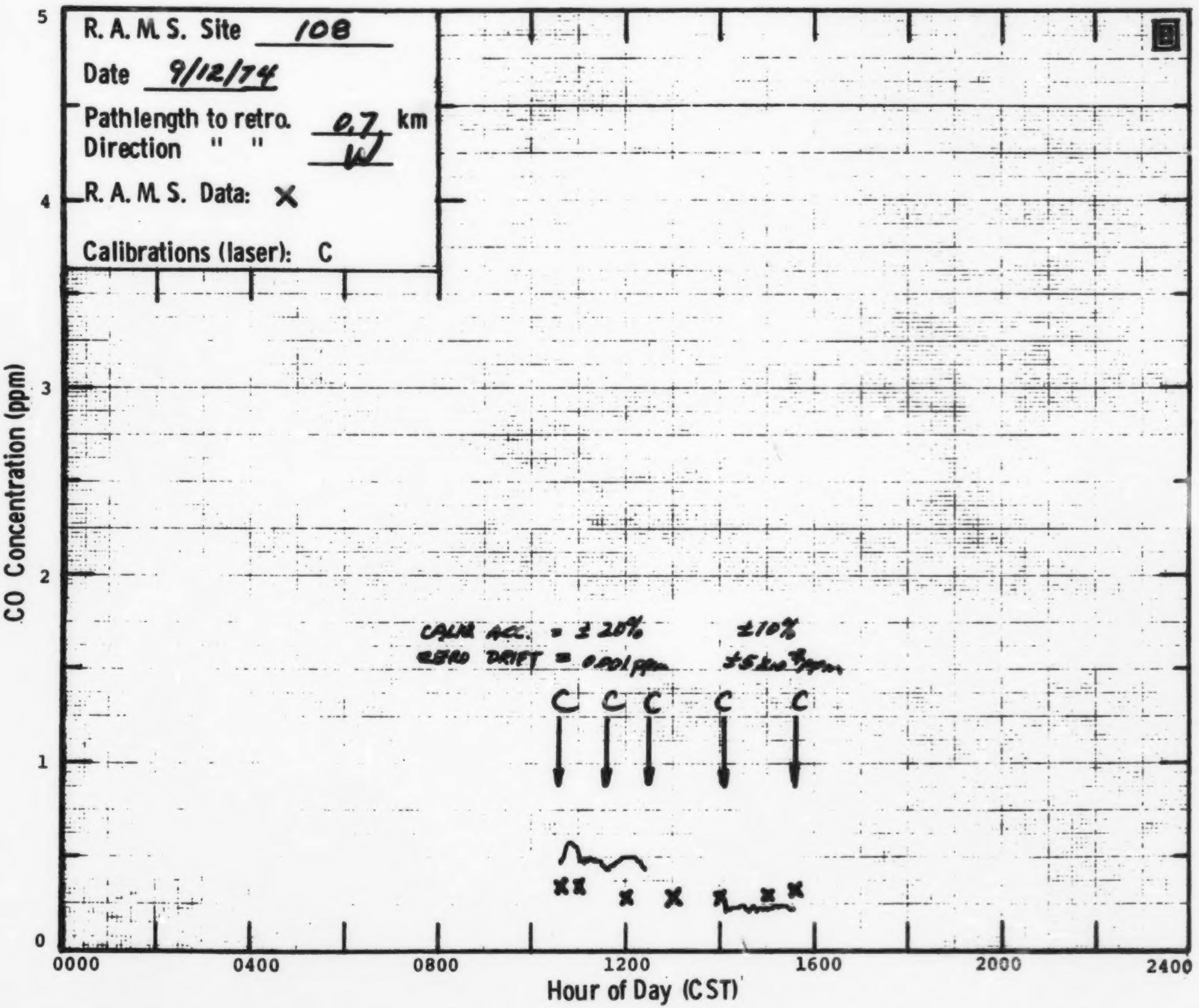
ZERO DRIFT = ± 0.04 ppm


R. A. M. S. Site 108
Date 9/10/74
Pathlength to retro. 0.25 km
Direction " " W
R. A. M. S. Data: X
Calibrations (laser): C
CALIB. ACC. = ± 5% ← ±10% →
ZERO DRIFT = ± 0.01 ppm ±0.05 ppm
C
C
C
X
X XX
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)



R. A. M. S. Site 108
Date 9/11/74
Pathlength to retro. 0.7 km
Direction " " W
R. A. M. S. Data: X
Bag sample: O
Calibrations (laser): C

CALIB. ACC. = ±15%
ZERO DRIFT = 0.0 ppm



R. A. M. S. Site 108

Date 9/12/74

Pathlength to retro. 0.7 km

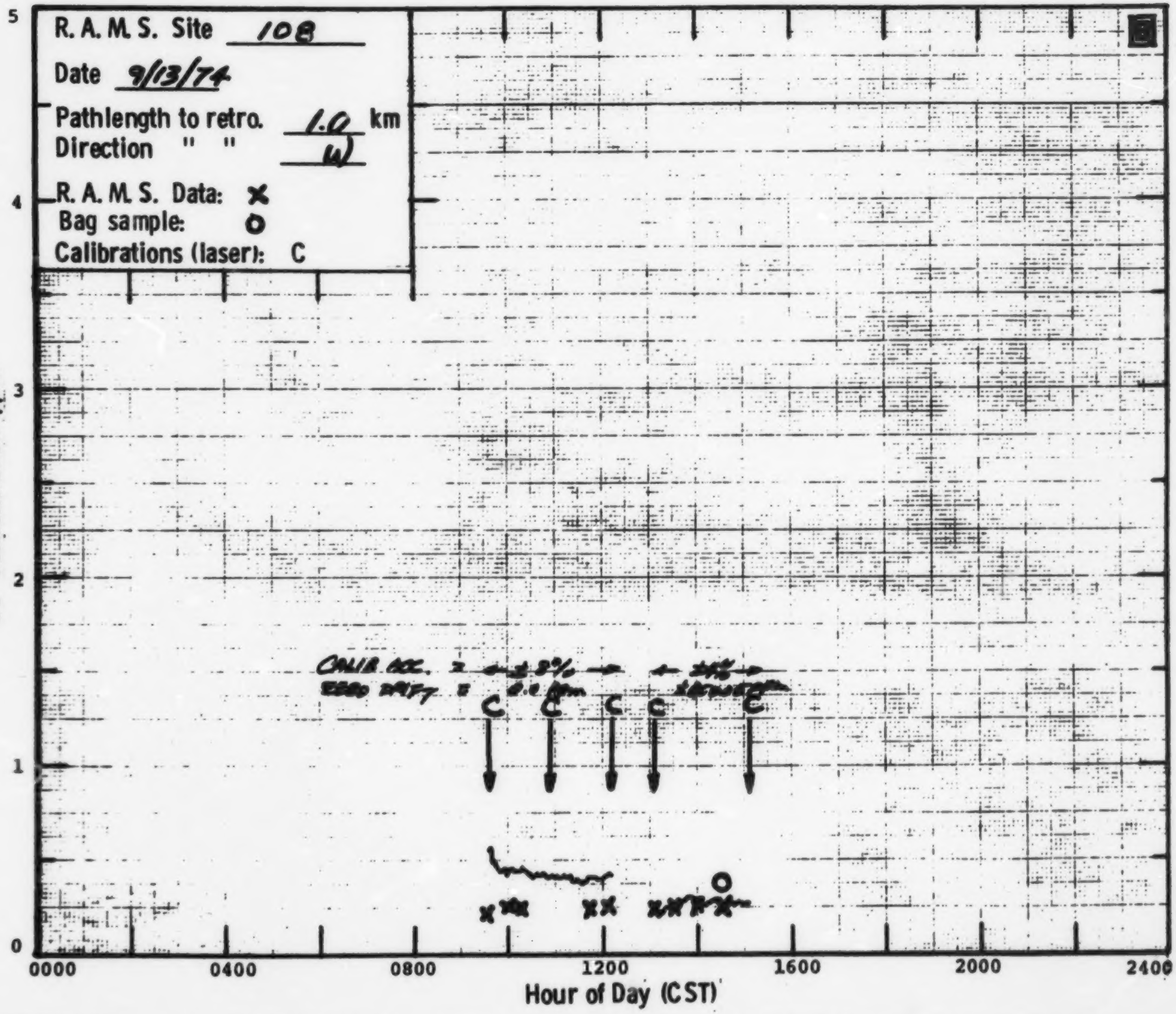
Direction " " W

R. A. M. S. Data: ×

Calibrations (laser): C

CALIB ACC. = ± 20% ±10%

ZERO DRIFT = 0.001 ppm $\pm 5 \times 10^{-3}$ ppm



R. A. M. S. Site 108

Date 9/13/74

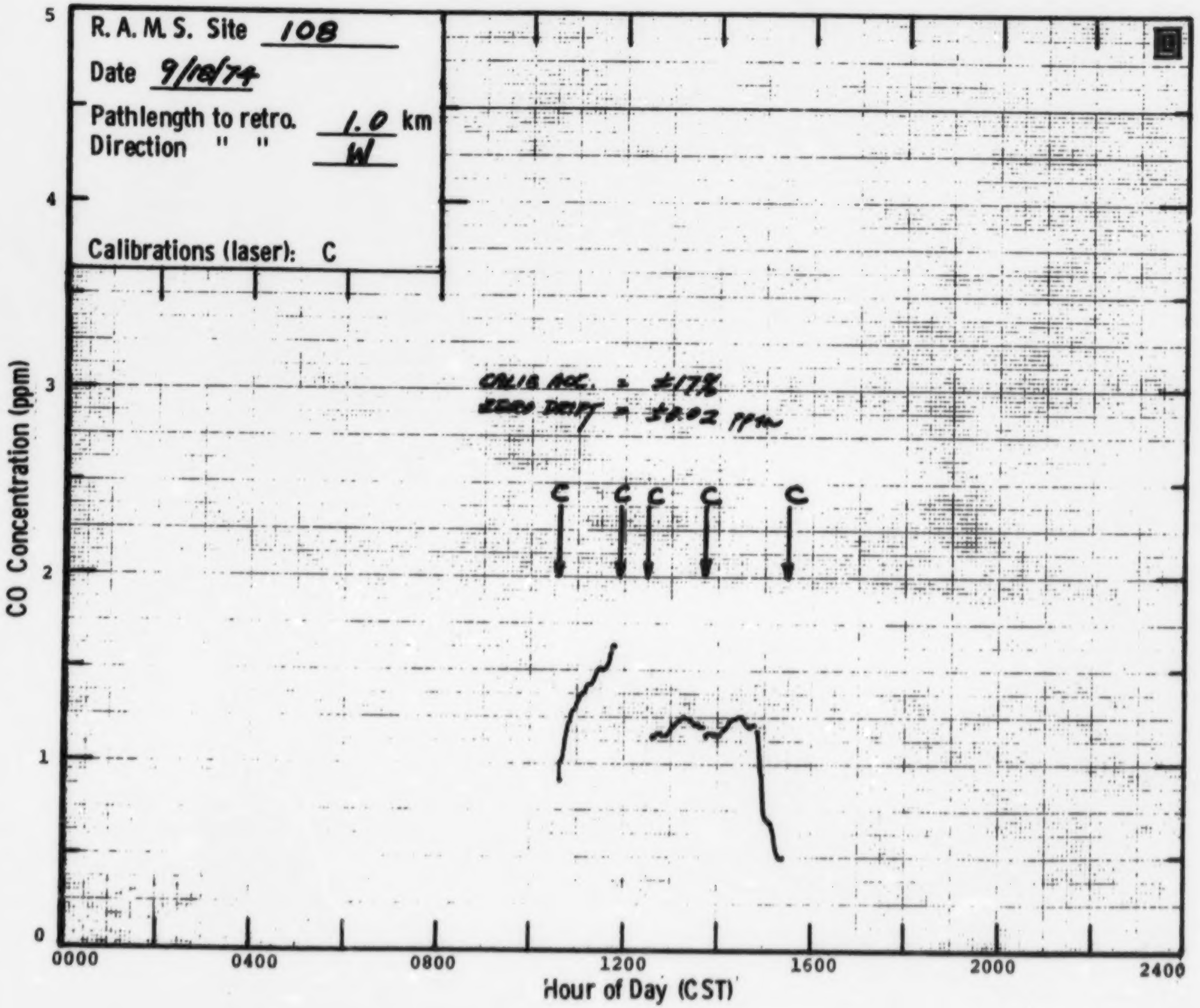
Pathlength to retro. 1.0 km

Direction " " W

R. A. M. S. Data: ×

Bag sample: o

Calibrations (laser): C



R. A. M. S. Site 108

Date 9/18/74

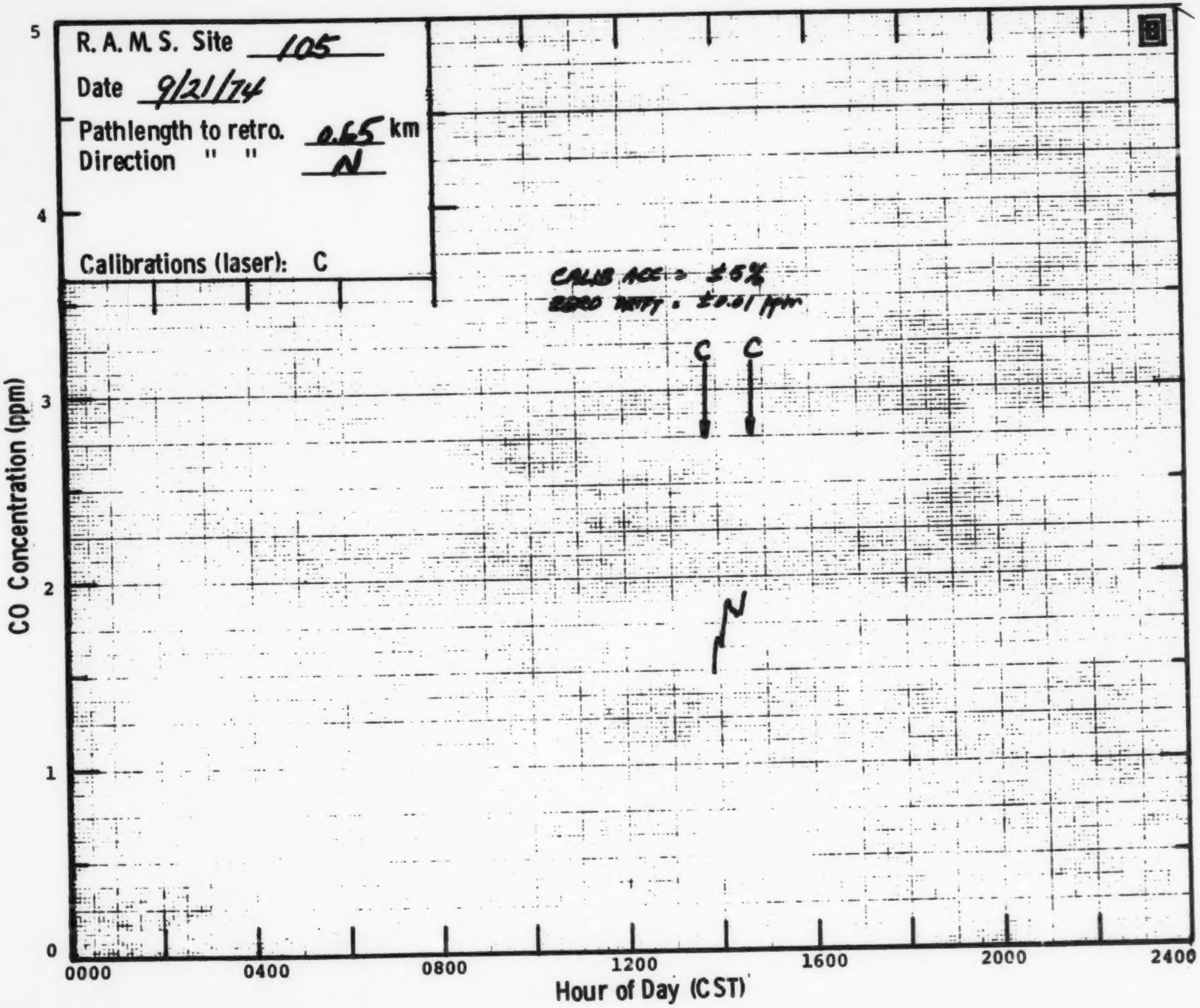
Pathlength to retro. 1.0 km

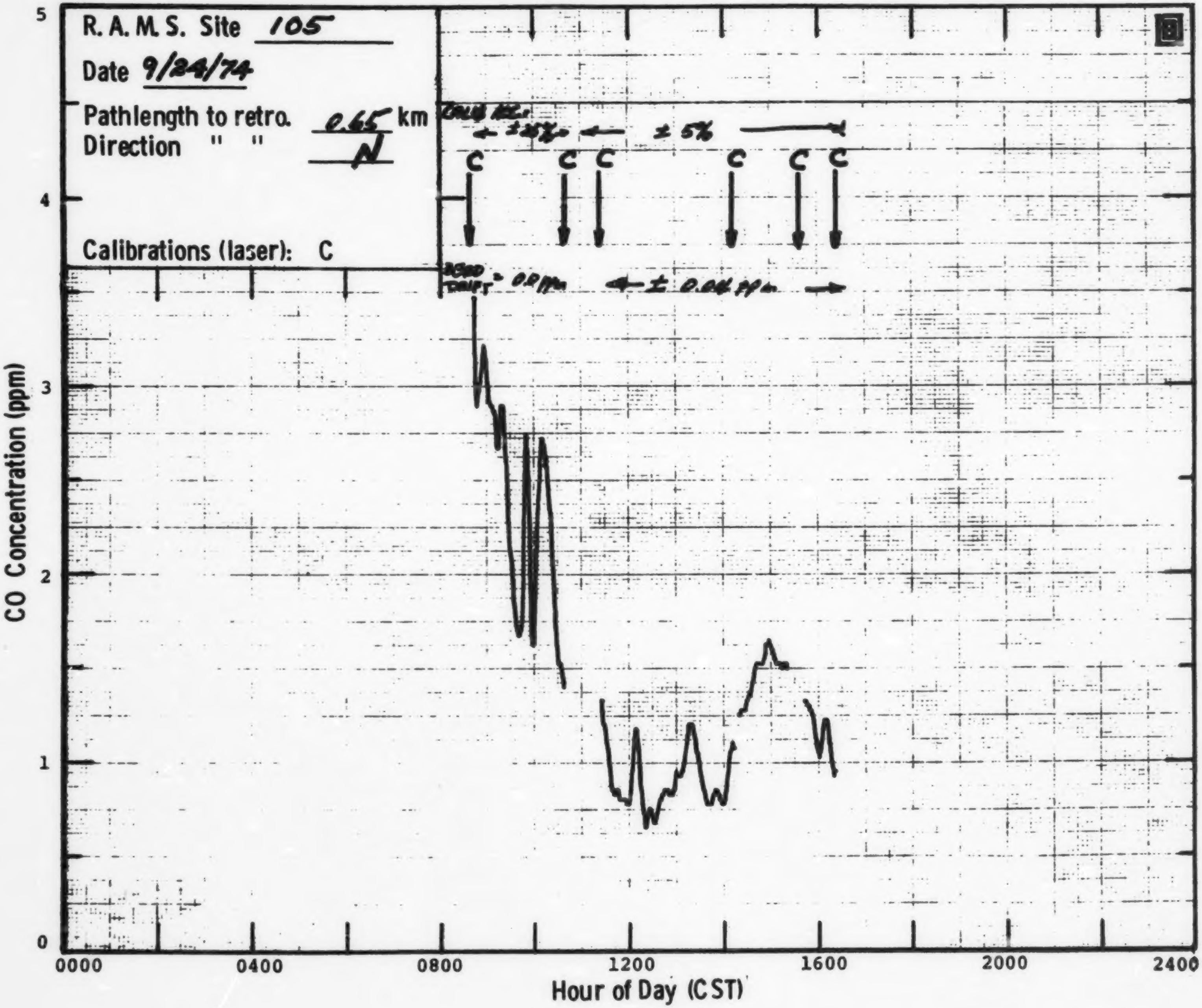
Direction " " W

Calibrations (laser): C

CALIB ACC. = ±17%

ZERO DRIFT = ±0.02 ppm





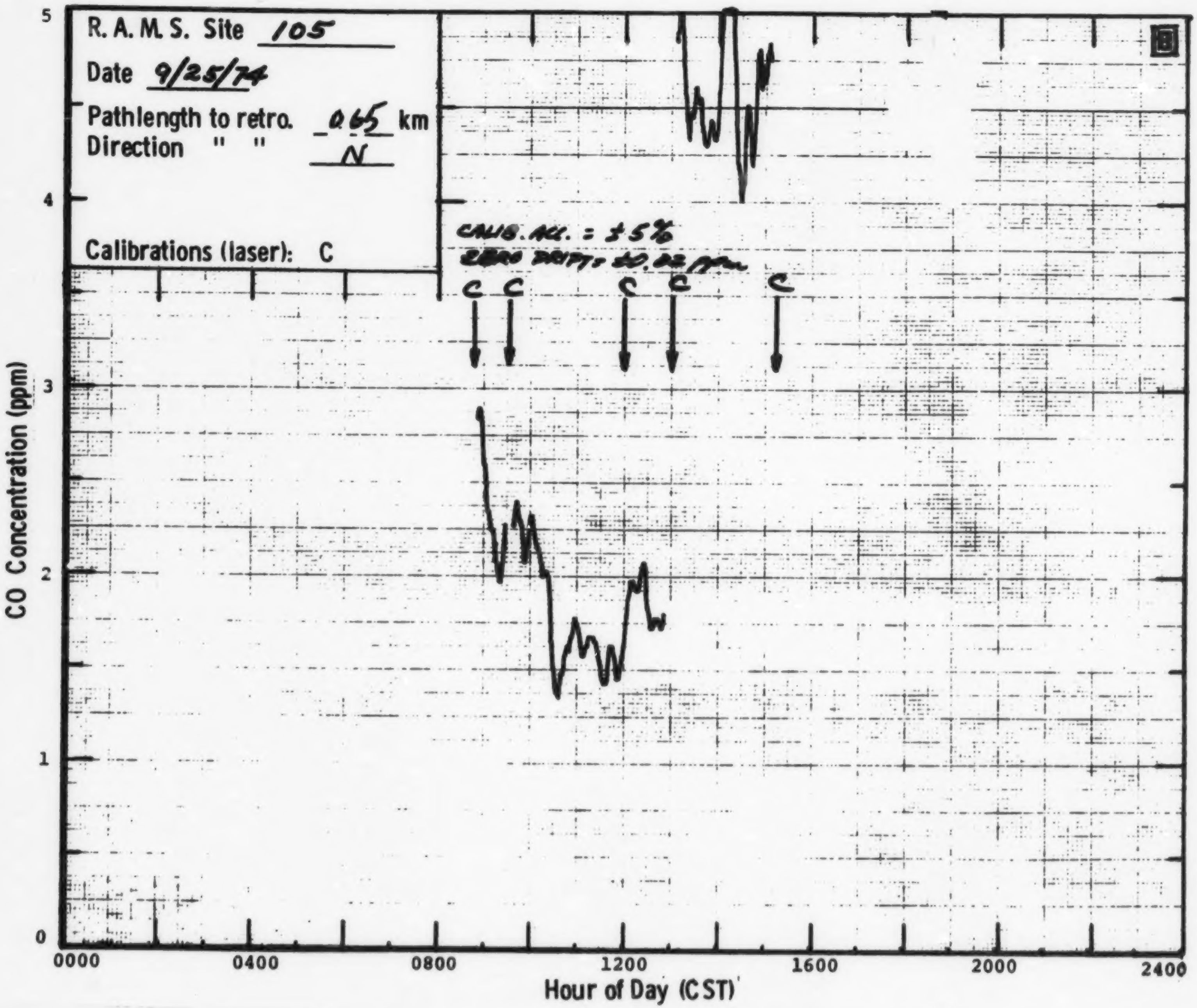
R. A. M. S. Site 105

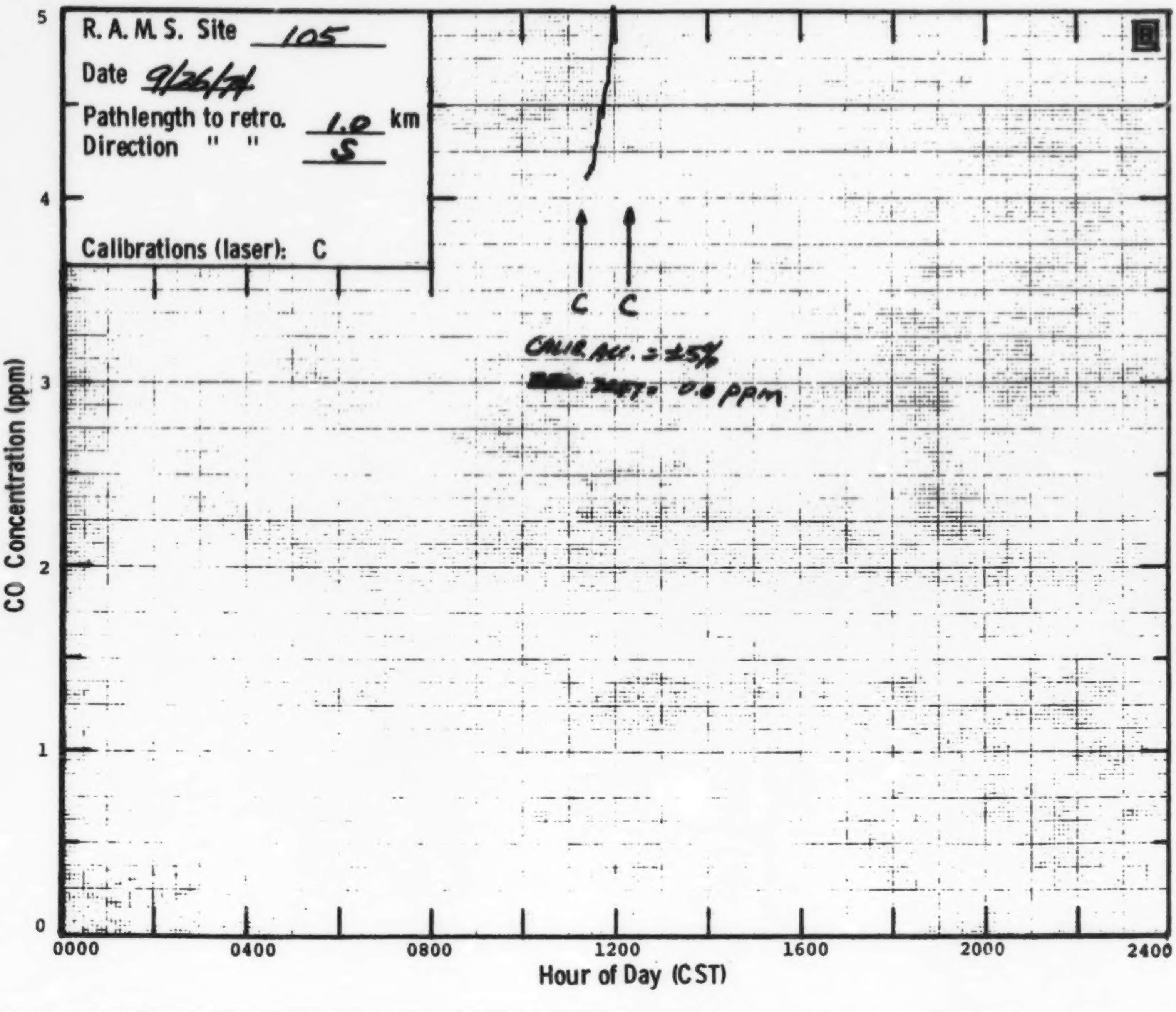
Date 9/24/74

Pathlength to retro. 0.65 km

Direction " " N

Calibrations (laser): C


R. A. M. S. Site 105
Date 9/25/74
Pathlength to retro. 0.65 km
Direction " " N
Calibrations (laser): C
CALIB. ACC. = ±5%
ZERO DRIFT = ±0.02 ppm
C C C C C
CO Concentration (ppm)
0
1
2
3
4
5
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)



R. A. M. S. Site 105

Date 9/26/74

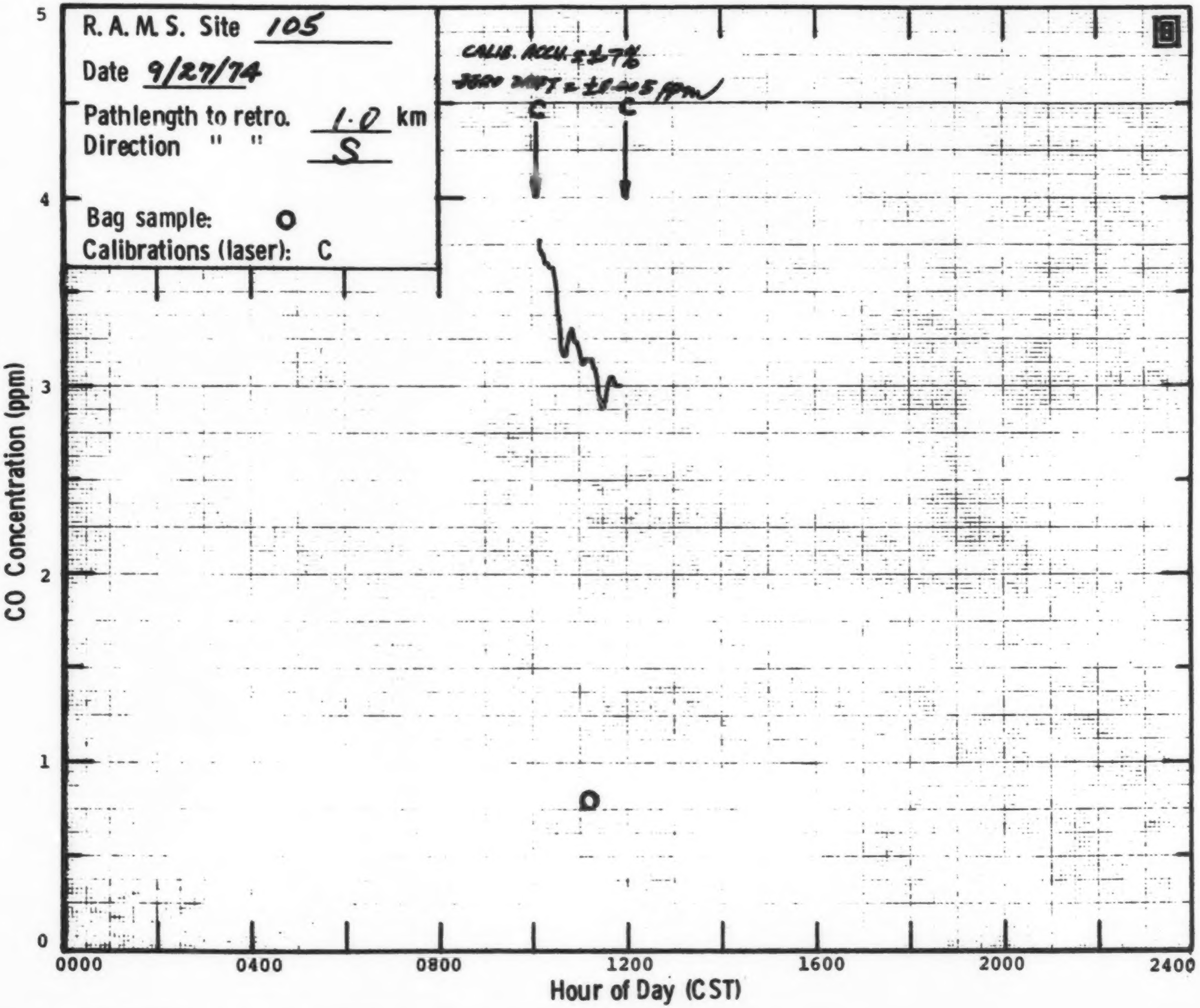
Pathlength to retro. 1.0 km

Direction " " S

Calibrations (laser): C

CALIB. ACC. = ±5%

[redacted] DRIFT = 0.0 ppm



R. A. M. S. Site 105

Date 9/27/74

Pathlength to retro. 1.0 km

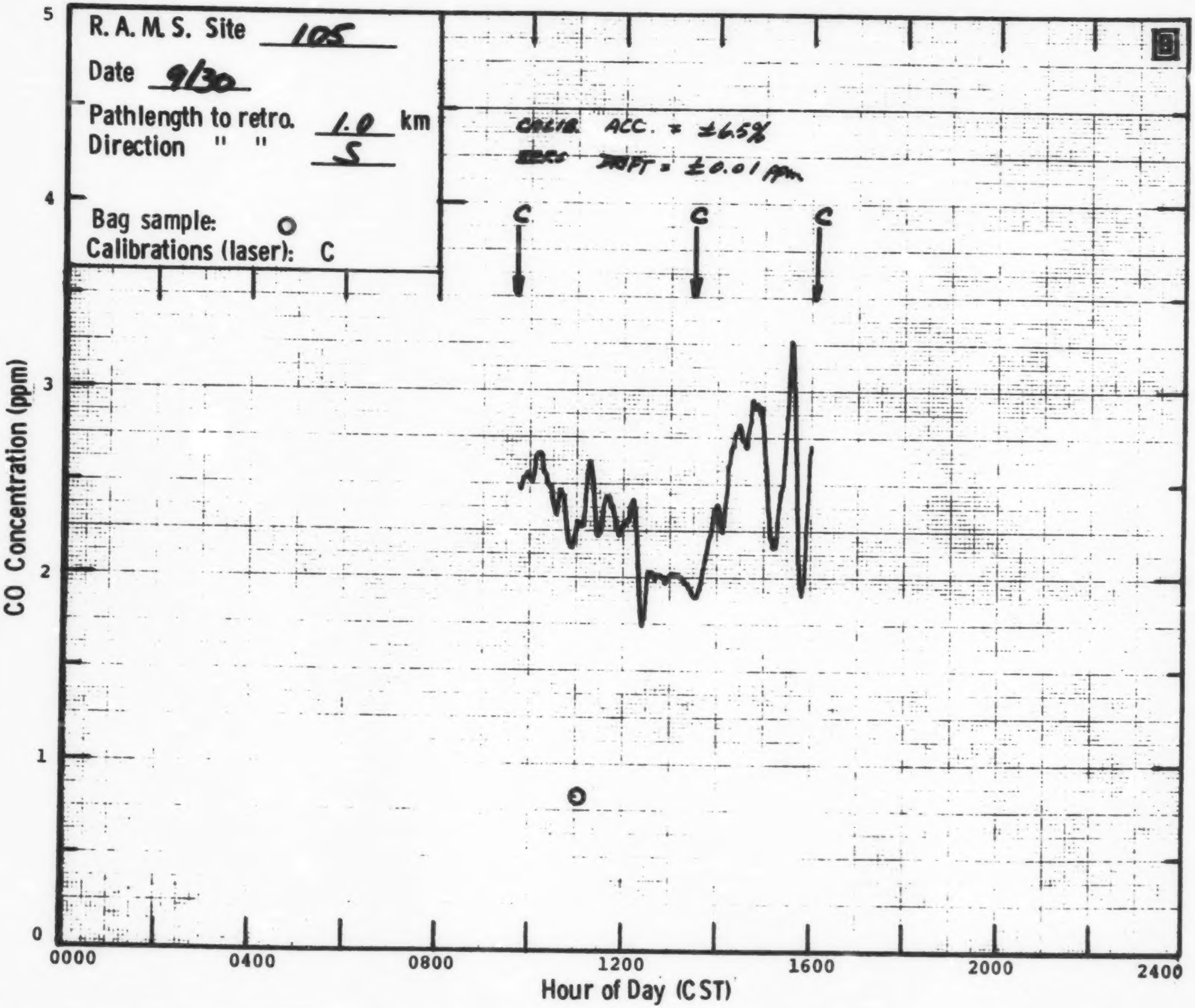
Direction " " S

Bag sample: ○

Calibrations (laser): C

CALIB. ACCU. = ±7%

ZERO DRIFT = ±0.05 ppm



R. A. M. S. Site 105

Date 9/30

Pathlength to retro. 1.0 km

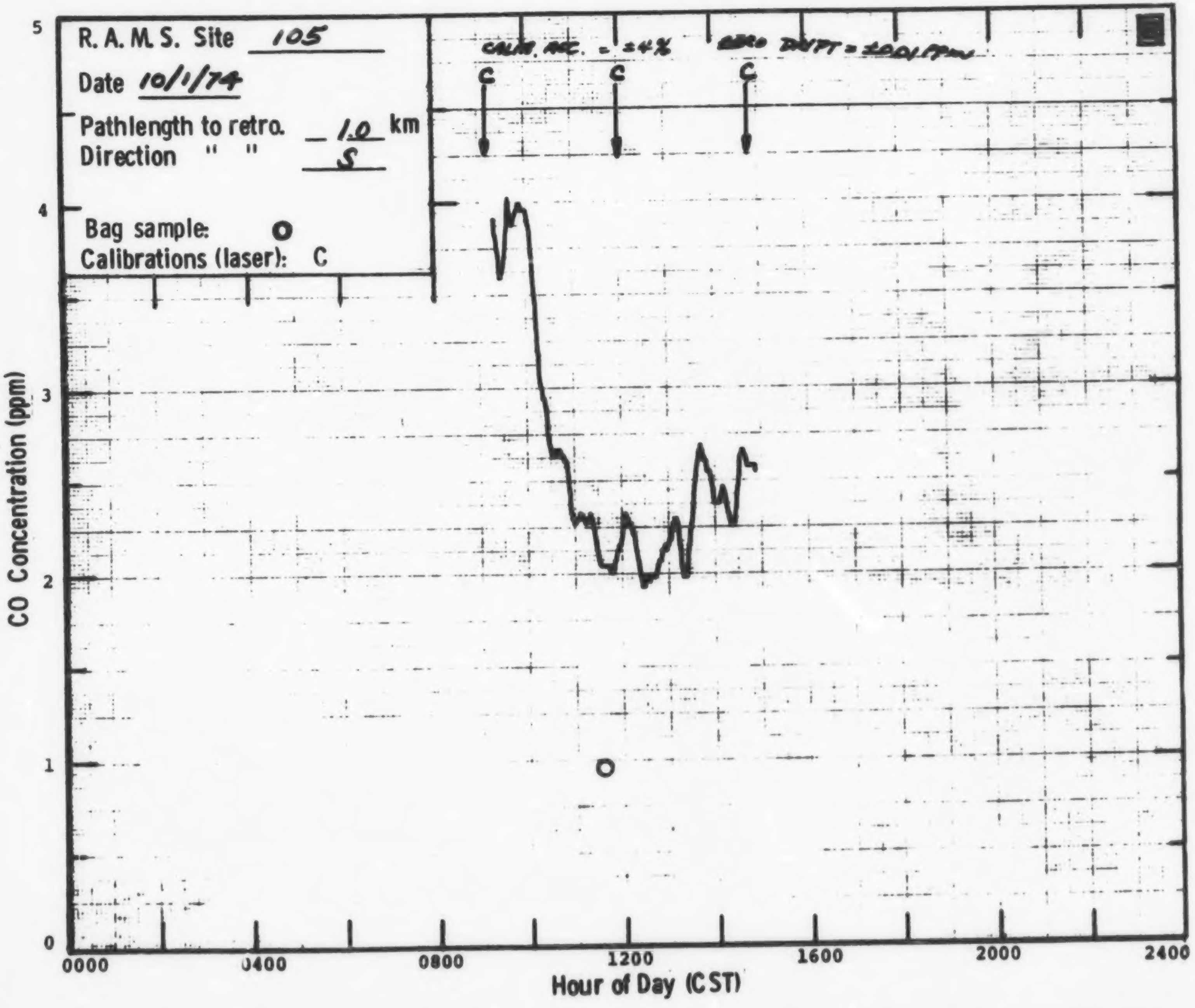
Direction " " S

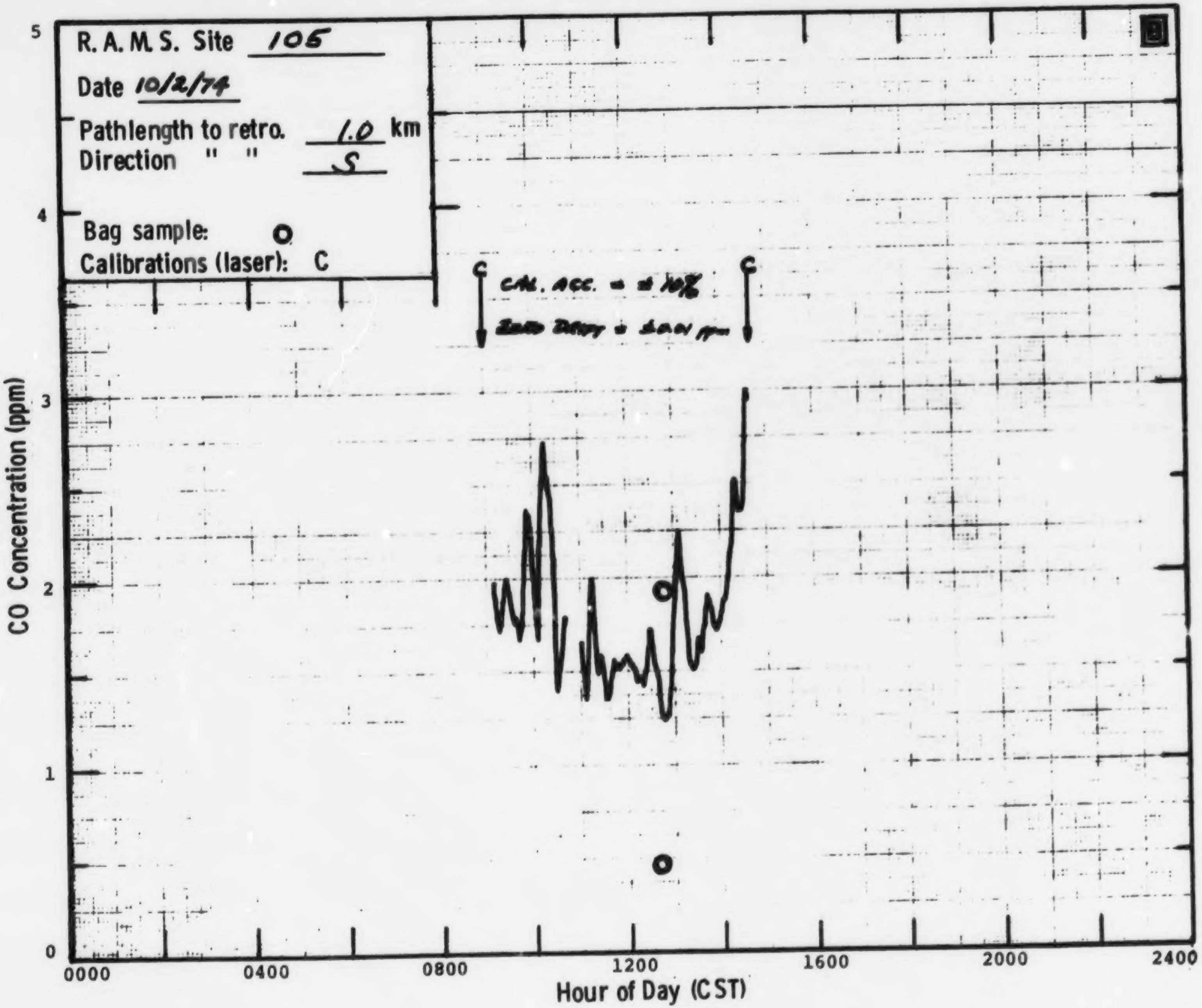
Bag sample: ○

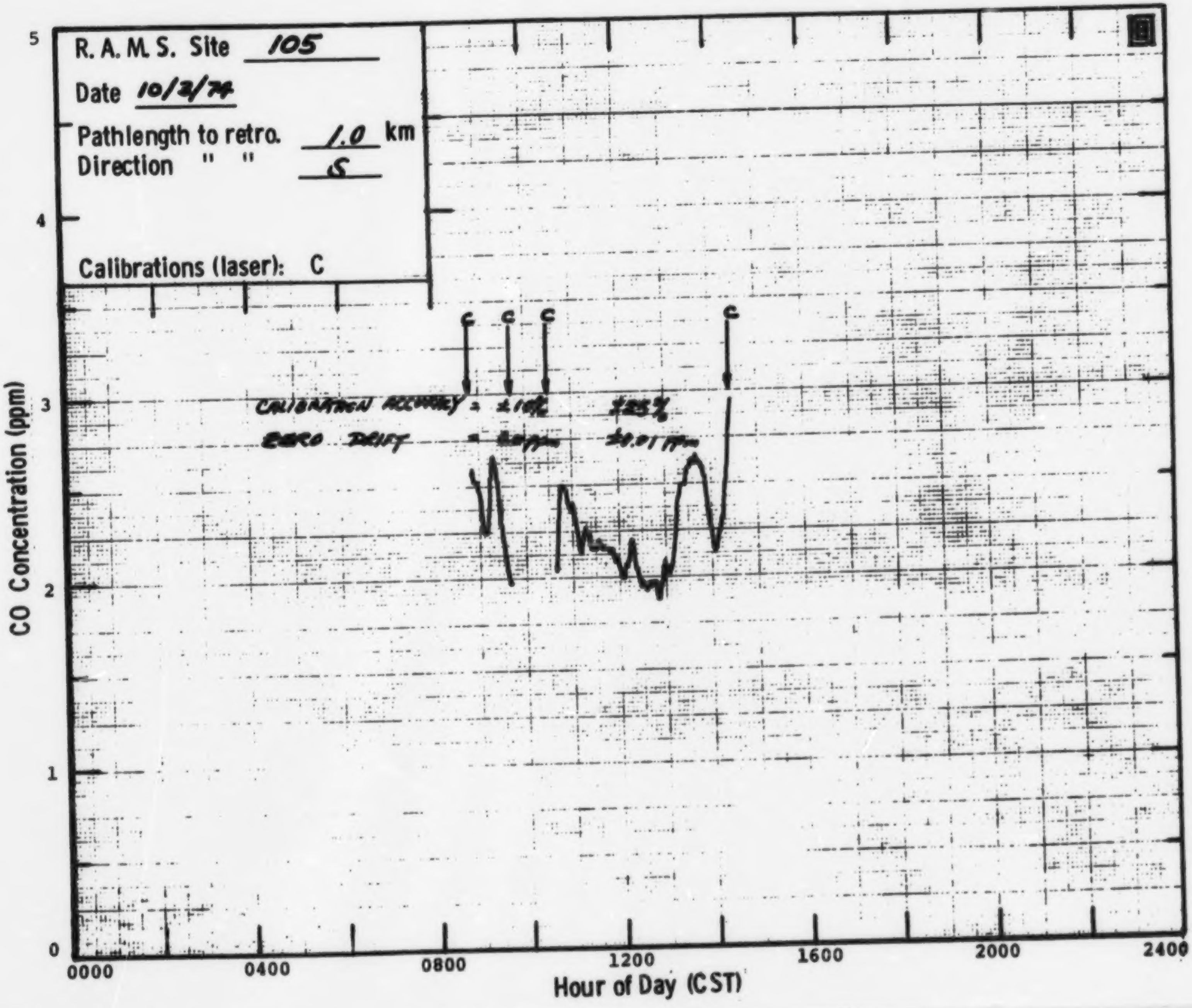
Calibrations (laser): C

CALIB. ACC. = ±6.5%

ZERO DRIFT = ±0.01 ppm


R. A. M. S. Site 105
Date 10/1/74
Pathlength to retro. 1.0 km
Direction " " S
Bag sample: O
Calibrations (laser): C
CALIB. ACC. = ±4%
ZERO DRIFT = ±0.1 PPM
C
C
C
5
4
3
2
1
0
CO Concentration (ppm)
0000
0400
0800
1200
1600
2000
2400
Hour of Day (CST)


R. A. M. S. Site 105
Date 10/2/74
Pathlength to retro. 1.0 km
Direction " " S
Bag sample: O
Calibrations (laser): C
C
CAL. ACC. = ± 10%
Zero Drift = ±0.01 ppm
C
CO Concentration (ppm)
0
1
2
3
4
5
Hour of Day (CST)
0000
0400
0800
1200
1600
2000
2400



APPENDIX C

Long-Path Monitoring of Atmospheric Carbon Monoxide with a Tunable Diode Laser System*

by

R. T. Ku, E. D. Hinkley, and J. O. Sample

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*Published in Applied Optics 14, 854 (1975).

LONG-PATH MONITORING OF ATMOSPHERIC CARBON MONOXIDE WITH A TUNABLE DIODE LASER SYSTEM*

by

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Lexington, Massachusetts 02173

Abstract

Long-path measurements of carbon monoxide in the atmosphere are described. The technique of resonance absorption was used in which the wavelength of radiation from a $PbS_{0.82}Se_{0.18}$ semiconductor diode laser was tuned into coincidence with an absorption line of CO in its fundamental band around 4.7 μm. By employing rapid frequency-modulation of the laser emission to overcome atmospheric turbulence effects it was possible to achieve a minimum detectable concentration of 5 parts per billion over a 0.61 km path. Continuous around-the-clock monitoring was also performed, and permitted increases in the ambient CO level due to commuter traffic to be observed.

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* This work was supported by the National Science Foundation (RANN) and the U. S. Environmental Protection Agency.

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I. INTRODUCTION

Several laser techniques are currently being developed and implemented for remote monitoring of the atmosphere.[1] The use of laser radar (lidar) involving detection of backscattered radiation from aerosols has advanced the furthest. Lidar is being used by Collis[2] and others[3] throughout the world to measure the dispersion of smoke plumes from factory stacks and the heights of temperature inversion layers, to mention just two applications. In 1969 Inaba and Kobayasi[4] suggested that there would be characteristic shifts in frequency of the backscattered radiation from pollutant gas molecules due to their Raman scattering signatures, and they pioneered the use of Raman lidar for remote detection of gases such as SO_2 and CO_2.[5] Unfortunately, Raman scattering cross-sections are quite small ($\sim 10^{-29}$ cm^2/str) and generally restrict this technique to the relatively high concentrations near pollutant sources. Recent measurements by Penney,[6] however, indicate that with tunable lasers it may be possible to improve the Raman scattering cross-sections by several orders of magnitude; resulting in sensitivities for certain molecules which may permit their detection in the ambient air by Raman lidar. Another technique of laser monotoring is based upon the principle of resonance fluorescence, where the absorption of laser radiation tuned to a particular transition of an atom or molecule produces subsequent re-radiation at another frequency characteristic of the specie. Using a tunable dye laser, Bowman et al[7] were able to detect sodium atoms at

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an altitude of 90 km at a concentration of 10^4 cm^{-3}. Gelbwachs et al[8] detected NO_2 in the lower atmosphere by resonance fluorescence; and in a review paper Kildal and Byer[9] predicted theoretically that CO could be detected by this technique using a tunable laser operating at 4.7 μm.

Each of the above laser monitoring techniques is monostatic, since no remotely-situated equipment is necessary; and, by time-gating analysis of the received signals, each provides range information. Their main limitations are as follows: lidar is limited primarily to aerosol detection; Raman lidar requires high-power tunable lasers for sensitive monitoring applications; and resonance fluorescence appears most useful for only a few atoms and molecules, requiring atmospheric "windows" at both the laser and fluorescent wavelengths.

Since the molecular cross sections for resonance absorption are relatively large ($\sim 10^{-18}$ cm^2 for strong lines in the infrared), and every pollutant gas has a characteristic absorption signature, consideration has recently been given to the use of resonance absorption for sensitive monitoring of gaseous pollutants.[10] In an attempt to retain the ranging and monostatic features of a lidar-type system, yet obtain the sensitivity of resonance absorption, Rothe et al[11] directed a dye laser beam into an urban atmosphere and detected the Mie-backscattered energy from the aerosols as the laser was tuned through a strong absorption line of NO_2. Concentrations of NO_2 as low as 50 ppb (parts per billion) were detectable at distances to 4 km. Resonance absorption using topographical reflectors was proposed in 1973 by Byer and Garbuny[12] as a useful technique for monitoring pollutant gases near the earth's surface. In 1974 they reported, with Henningsen, the detection of CO using an optical parametric oscillator tuned to the 2.3-μm overtone of this molecule and backscattering from natural foliage.[13]

In this paper we describe a bistatic laser system for sensitive detection of CO by resonance absorption at 4.7 μm over an outdoor path of 0.61 km.* Such integrated-path measurements are important for studying various computer models being proposed for region-wide prediction of pollution levels, since their basic grid size is usually around 1 km.[14] Thus the long-path measurements can provide both the input pollution data and the final data for evaluation of these models which take into account meteorological and topographical parameters as well. The use of a remote retroreflector permits low, safe laser power levels to be used (less than 1 mW), which is particularly important for measurements made near eye level. The heart of this system is a $PbS_{0.82}Se_{0.18}$ semiconductor diode laser which can be current-tuned[15] into coincidence with specific absorption lines of CO within the 2145-cm^{-1} fundamental band.[16] Atmospheric turbulence effects were reduced considerably by frequency-modulating the laser emission at 10 kHz and dividing the resulting derivative signal by the direct transmission.

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* The pathlength has recently been extended to 2 km in preliminary experiments performed in St. Louis, Missouri during the first Regional Air Pollution Study of the U, S. Environmental Protection Agency. These results will be reported in a future article.

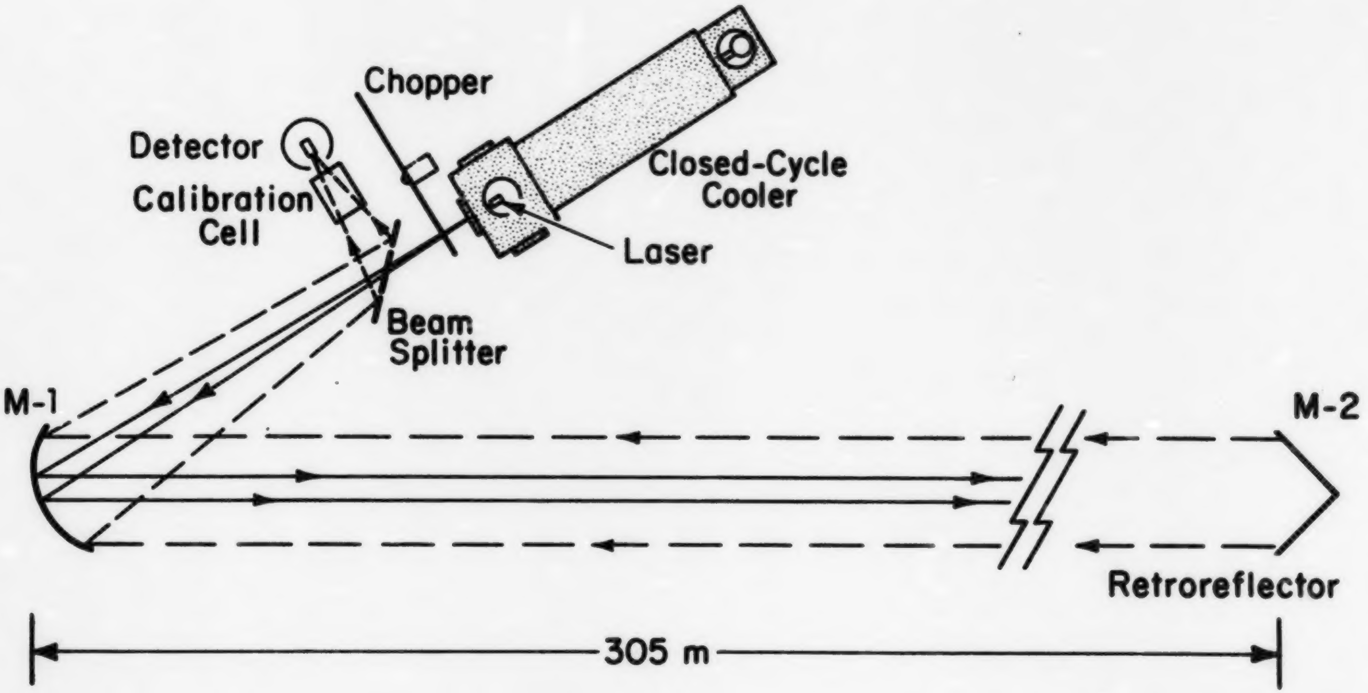
Chopper
Detector
Calibration Cell
Closed-Cycle Cooler
Laser
Beam Splitter
M-1
M-2
Retroreflector
305 m

Fig.C-1. Schematic of laser and optical system for long-path monitoring of atmospheric pollutant gases.

Carbon monoxide is a dangerous pollutant present in the atmosphere today, especially in metropolitan areas where the density of automobiles is high (the CO content of automobile exhaust can be as high as 10% by volume). In addition to its harmful and poisonous effects, CO plays an important role in the formation and conversion of other pollutants such as NO, O_3, and NO_2.[17] Traditionally, the amount of CO in the air has been measured by point-sampling instruments using conventional infrared or gas-chromatographic techniques. The limitations of these methods become obvious in cases where the average values of pollutant concentration over an extended area are desired; and the long-path tunable laser system described here represents a development in the direction of a versatile, remote, and reliable air-monitoring system for such applications.

II. FIELD MEASUREMENT SETUP

Measurements were performed at the Lincoln Laboratory antenna range located on the western side of Hanscom Field in Bedford, Massachusetts. The range is 305 meters long, with small buildings for equipment at each end. One building contained the laser system and the other a hollow corner-cube retroreflector. A concrete floor provided vibrational stability for the laser system.

The essential components of the optical system are sketched in Fig.C-1. The $PbS_{0.82}Se_{0.18}$ semiconductor diode laser was mounted inside a closed-cycle cryogenic cooler which required only electrical power to maintain operating temperatures down to 10 K within an accuracy of 0.001 K.[18] This temperature control provides an additional tuning mechanism for the diode laser (in addition to current tuning) and better mode selection. A more detailed description of the cooler and laser operation will be given in another publication.[19] The laser beam was collimated by an off-axis, aluminum-coated parabolic mirror (M-1) 12 cm in diameter and transmitted across the 305-m path to a corner-cube retroreflector (M-2) of the same size. The return beam was reflected from the collimating mirror to a Ge beam-splitter, finally impinging on the liquid-nitrogen-cooled InSb infrared detector. The best overall efficiency for this optical arrangement, taking into account the beam-splitter losses, was 40%.

III. MEASUREMENT AND CALIBRATION TECHNIQUES

Tunable laser experiments have been performed in various laboratories to determine absorption coefficients, linewidths, and lineshapes of atomic and molecular transitions.[20] When tunable diode lasers are used for such measurements the absorbing medium is in a cell between the laser and infrared detector, with a spectrometer usually in the path for mode separation and wavelength calibration. The diode laser frequency ν is swept through the molecular absorption line by varying the direct (injection) current through the laser. An x-y recorder whose x-axis is proportional to diode current (usually linear with ν over small increments) is used to record the transmission dip $P_o \exp\left[-\alpha(\nu)CL\right]$, where P_o is the power received in the absence of gas in the cell, $\alpha(\nu)$ is the frequency-dependent absorption coefficient in cm^{-1}/ppm, C is the gas concentration in ppm, and L is the cell length in cm. By this technique $\alpha(\nu)$ can be measured in the laboratory for known gas concentrations and the values used to determine pollutant levels on the basis of similar measurements made in the field.

For long-path atmospheric monitoring it is important to select the best absorption line of the molecule to be detected within the most appropriate atmospheric transmission "window." Figure C-2 shows a computed transmission spectrum of a typical atmosphere around 4.7 μm for a 10-km path.[21,22] Superimposed on this spectrum are the locations of strong CO absorption lines in this region, whose relative strengths are indicated by the lengths of the vertical lines. Since most of the atmospheric interferences in this region would normally be due to water vapor, CO lines furthest from H_2O absorption, such as the P(3) or P(4) would appear to be most appropriate for monitoring. In order to observe the actual shape of the CO absorption lines as they appear in the atmosphere, diode laser scans were performed in the manner indicated above on the P(1) through P(8) transitions. Fig. C-3 illustrates an experimental laser scan of the P(5) line centered at 2123.7 cm^{-1}, broadened with one atmosphere of air. The dashed line is a theoretical Lorentzian fit to the experimental scan using a peak absorption constant of

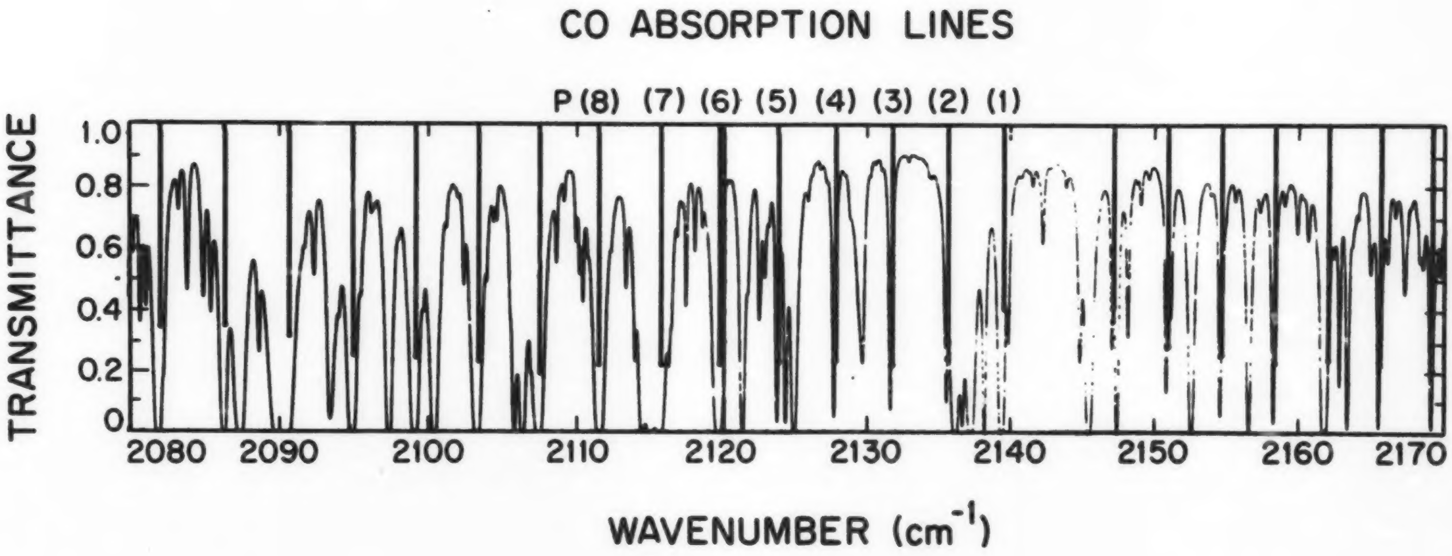

Fig.C-2. Computed atmospheric transmission spectrum around 4.7 μm for 10 km path (after Refs.21 and 22). Heavy vertical lines show locations and relative strengths of the strong CO lines in this region.

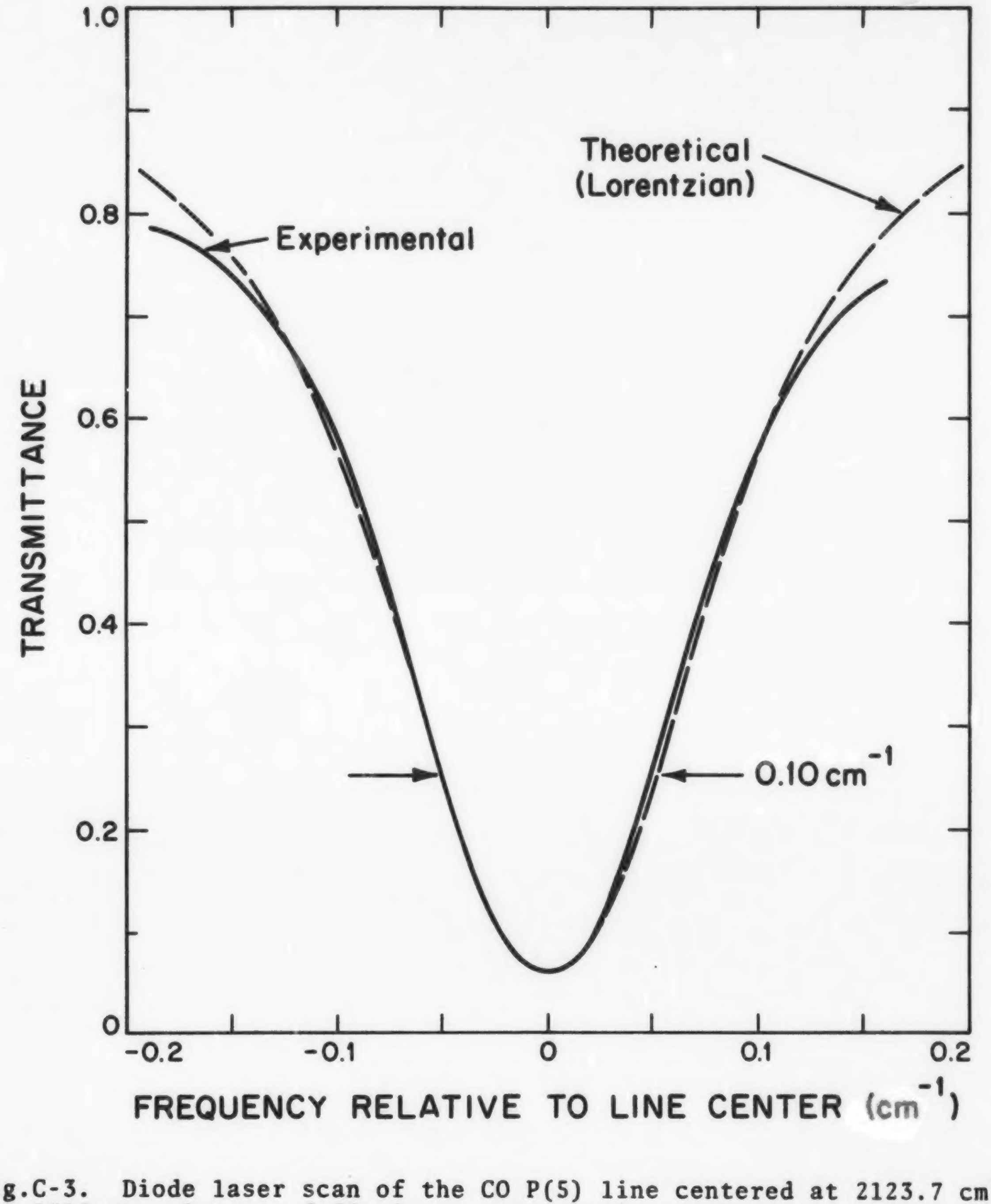

Fig.C-3. Diode laser scan of the CO P(5) line centered at 2123.7 cm^{-1}, for 1316 ppm mixture of CO:air at atmospheric pressure in a 30-cm cell. The dashed line is a Lorentzian fit using $\alpha_o = 7.1 \times 10^{-5}\ cm^{-1}$/ppm and $2\gamma = 0.1\ cm^{-1}$.

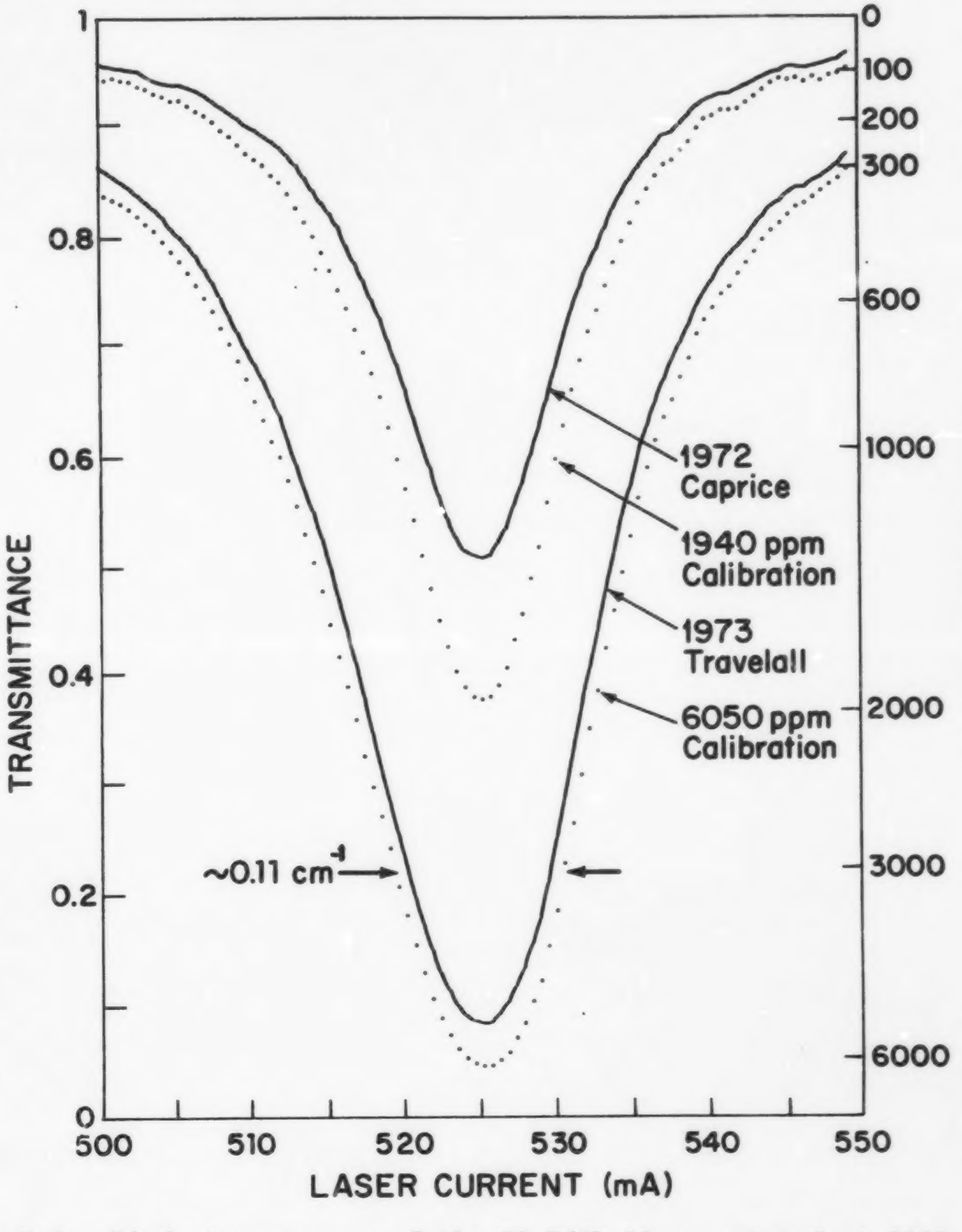

Fig.C-4. Diode laser scans of the CO P(7) line centered at 2115.6 cm^{-1} for specimens of raw automobile exhaust in a 10-cm cell. The solid lines represent data from a 1972 Chevrolet Caprice and a 1973 International Travellall; the dotted curves represent scans of pure CO in N_2 at mixing ratios indicated.

7.1 x 10^{-5} cm^{-1}/ppm and FWHM (full width at half maximum absorption coefficient) of 0.10 cm^{-1}. There is clearly excellent agreement between the experimental lineshape and the theoretical Lorentzian curve.

In order to uncover potential interferences, all of the above CO lines were scanned in samples of raw automobile exhaust. Fig. C-4 illustrates diode laser scans of the P(7) line, centered at 2115.6 cm^{-1}, for exhaust samples from a 1972 Chevrolet Caprice and a 1973 International Travelall. For comparison, two calibrated mixtures of pure CO in N_2 were used, and are indicated by the dotted curves. Because of the lack of any significant differences in shape between the solid and dotted curves, we conclude that there is negligible interference from water vapor and other constituents of automobile exhaust in this region; and similar results were observed for the other CO lines as well. Consequently, any of these lines can be used for detection of CO in the atmosphere barring unexpected interferences by other molecules not present in automobile exhaust. Table I summarizes the absorption line parameters obtained for various CO transitions by diode laser spectroscopy in the laboratory.

Field measurements of gaseous pollutants in the ambient air differ from the laboratory measurements in two important respects: (1) no spectrometer is used to isolate a particular laser mode; and (2) the outdoor path cannot be evacuated as can an absorption cell. In most instances the diode laser emits

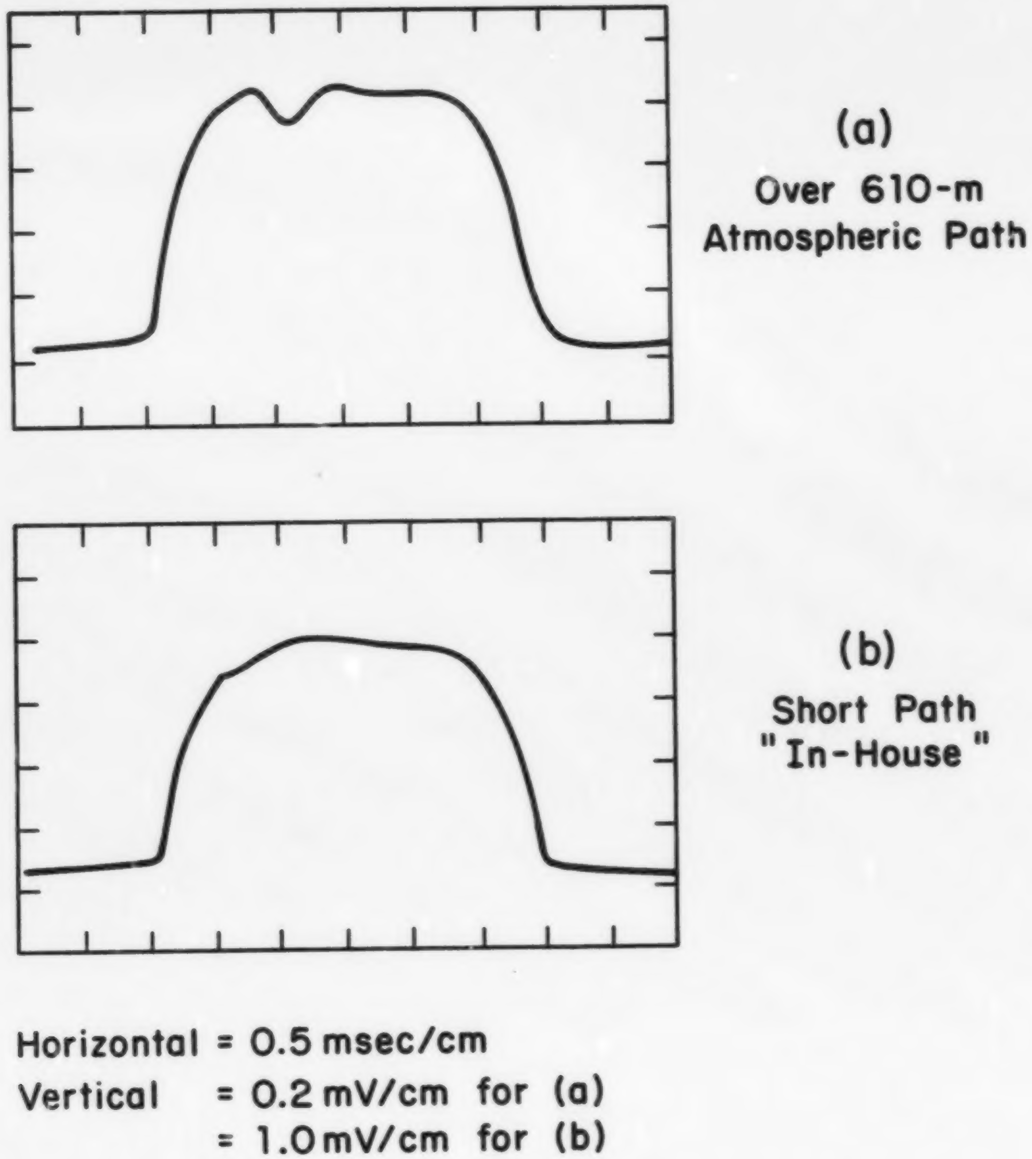

Fig.C-5. Oscillogram of (a) long-path (0.61 km) transmission showing dip at CO P(7) line resulting from ambient level of this gas, and (b) short-path comparison.

radiation primarily in a single mode, but in cases where there may be two modes of comparable intensity there will be a nonlinearity in the calibration in the absence of a spectrometer for isolation. Because of the strength of the CO absorption lines listed in Table I and the relatively high concentration of this pollutant in the atmosphere (usually above 0.1 ppm), transmission intensity dips due to resonance absorption were easily observed for the 0.61-km path (round-trip distance between laser and retroreflector). Fig. C-5(a) shows an oscillograph of the return signal versus time (wavelength) during a sinusoidal current pulse on the laser, and shows the transmission dip caused by ambient CO in the atmosphere. Fig. C-5(b) is a similar trace obtained when a retroreflector is placed just beyond the collimating mirror (M-1 in Fig. 1) so that the effective pathlength (or CO concentration) is essentially zero. This technique was used to obtain the "zero-pollutant" calibration for the field experiments described below.

Thermal fluctuations in the atmosphere were the main causes of noise in the received laser signal; and the problems of beam defocusing and steering have been reported for other laser systems as well.[23] We found the best signal stability on cloudy or rainy days when the temperature variation over the outdoor path was small. In order to perform a systematic study of the time dependence of amplitude scintillation over the path, we transmitted identical pulses (within 1% in amplitude) toward

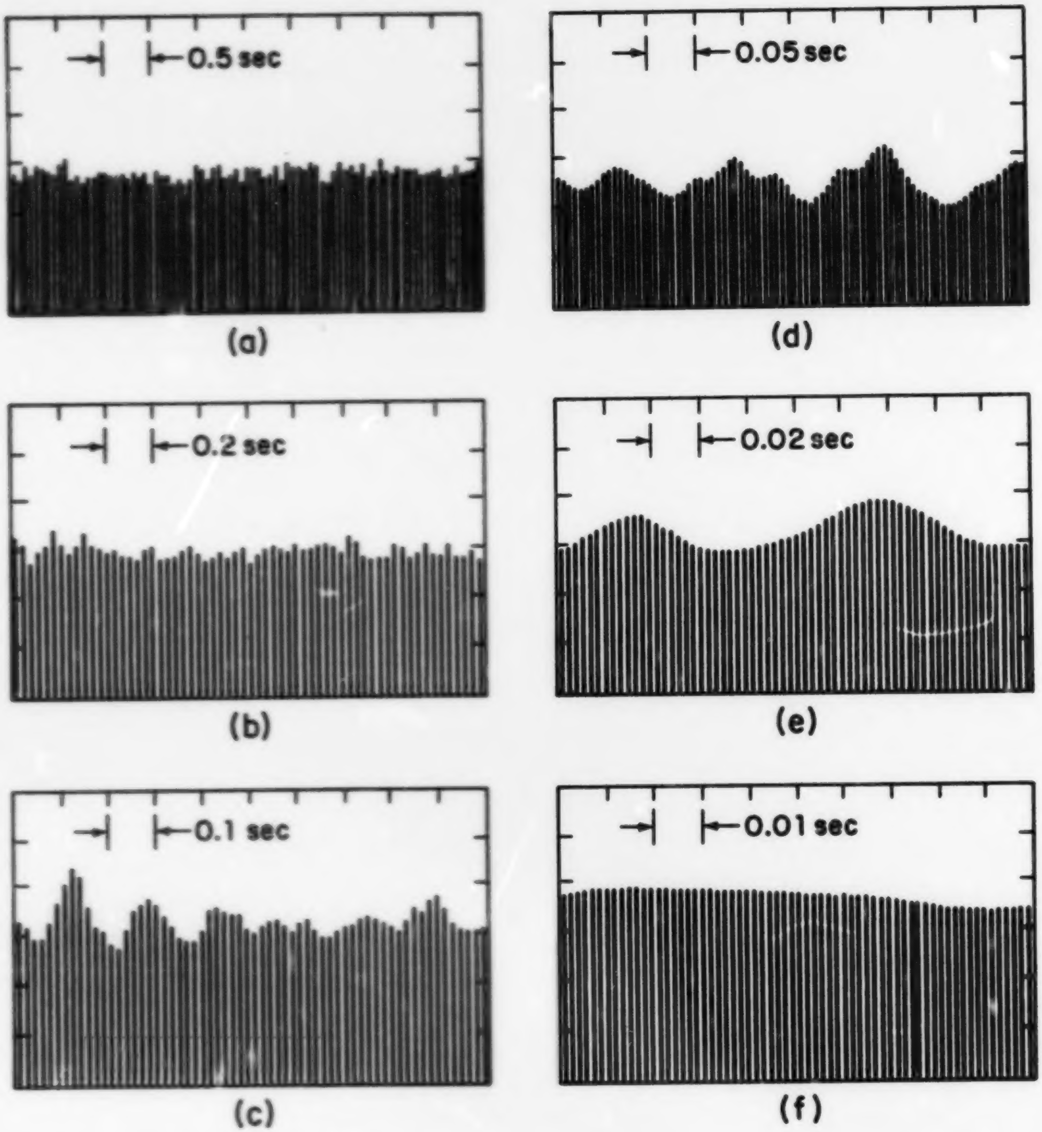

Fig.C-6. Pulse-to-pulse fluctuations during atmospheric transmission as repetition frequency varied as follows: (a) 17 Hz; (b) 31 Hz; (c) 63 Hz; (d) 166 Hz; (e) 325 Hz; (f) 650 Hz.

the retroreflector and observed the pulse-to-pulse variation in the detected laser power as the time between pulses was reduced from 59 msec to 1.5 msec. In Fig.C-6 are shown oscillograms corresponding to the six different pulse repetition rates used, with the pulse-to-pulse variation becoming negligible as the repetition rate became high enough to "freeze" the atmosphere.

In order to monitor trace gases over long atmospheric paths with high sensitivity, we developed a technique of fast derivative spectroscopy. The derivatives of absorption spectra similar to that of Fig.C-5(a) were obtained by modulating the diode current at 10 kHz (~20 mA peak-to-peak) around its steady current of 350-400 mA; and with synchronous detection at this frequency the short-term turbulence and scattering effects are reduced considerably, as indicated in Fig. C-6. The longer-term effects of beam-steering or extinction from aerosol clouds along the path, which affect the derivative signal as well as the direct transmission, are eliminated by dividing the derivative signal by the transmitted signal obtained from a lock-in amplifier tuned to the 170-Hz frequency of the mechanical chopper in Fig. C-1. In Fig.C-7(a) is shown a typical set of direct transmission scans of the P(4) CO line during both laboratory calibration and field monitoring over the 0.61-km path. In Fig. C-7(b) are scans of the first derivative under the same conditions. Mathematically, the received laser power P_r can be expressed as

$$P_r = P_o \exp\left[-\alpha(\nu)CL\right] \exp\left[-\beta(t)\right] , \tag{1}$$

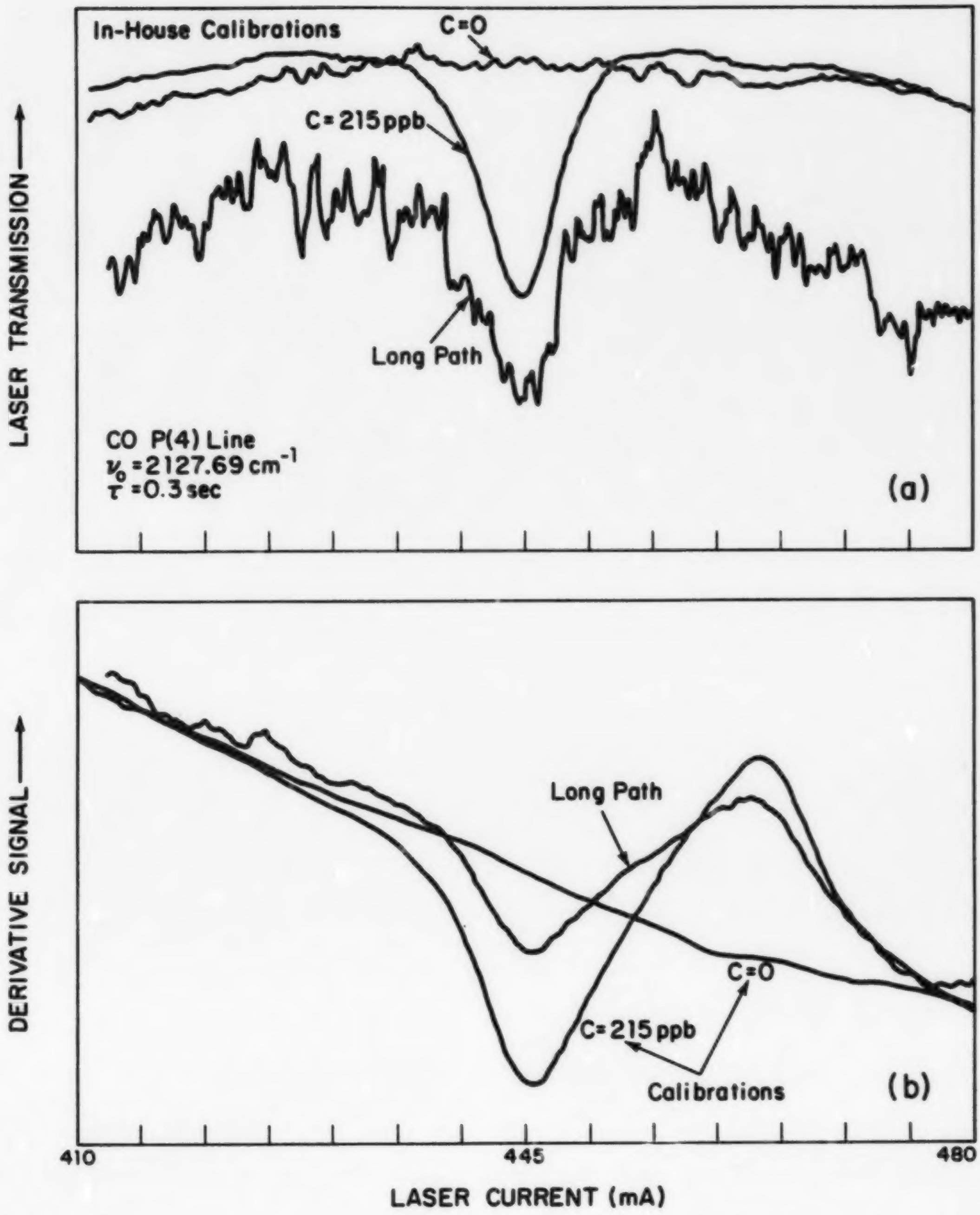

Fig.C-7. (a) Scans of CO P(4) line at 2127.7 cm^{-1} for 215 ppb calibration and for 0.61 km long-path measurement; (b) first derivative scans using 10-kHz frequency modulation of diode laser. (The small shift in (b) toward higher currents is caused by the added sinusoidal current.)

where $\beta(t)$ is an extinction parameter for extranneous effects such as atmospheric turbulence and aerosol scattering which are not related to the CO concentration. The other symbols were defined earlier. Since turbulence and scattering are not strongly wavelength dependent, $\beta(t)$ is essentially independent of ν over the small frequency increments used during laser monitoring. The derivative signal can be derived from Eq. (1):

$$dP_r/d\nu = -P_o C L \exp\left[-\alpha(\nu) C L\right] \exp\left[-\beta(t)\right] d\alpha(\nu)/d\nu. \tag{2}$$

As shown above, for CO absorption lines in the atmosphere, $\alpha(\nu)$ is Lorentzian and can be expressed as

$$\alpha(\nu) = \alpha_o/\left[1 + (\nu'/\gamma)^2\right] \tag{3}$$

where α_o is the absorption coefficient at line center, 2γ is the FWHM in the atmosphere, and $\nu' = \nu - \nu_o$ where ν_o is the center frequency for the particular transition. Using Eq. (3), the ratio between the first derivative signal of Eq. (2) to the direct transmission signal of Eq. (1) becomes

$$P_r'/P_r = \frac{2\,\alpha_o\,L\,\nu'}{\gamma^2\left[1 + (\nu'/\gamma)^2\right]^2} C , \tag{4}$$

whero $P_r' \equiv dP_r/d\nu$. Notice that the time-dependent turbulence and scattering parameter $\beta(t)$ has been eliminated, and that for a fixed nominal value of ν' the resulting signal is directly proportional to the pollutant gas concentration C . For maximum sensitivity the ratioed signal should be evaluated at a laser frequency where the slope of the absorption line is greatest. The only exception is when the pollution burden is so high that most of the laser power is absorbed within γ of line center. In such instances a weaker (possibly isotope) line can be selected or the nominal laser frequency can be tuned further away from line center.

A strip-chart recorder displaying a voltage proportional to the ratioed signal of Eq. (4) provided a continuous record of the average CO concentration along the path of the laser beam. Calibration was achieved by filling the 10-cm cell shown in Fig. 1 with different concentrations of CO in N_2 at atmospheric pressure. Since the length ratio between the outdoor path (0.61 km) and gas cell is 6100, a calibration cell concentration of 3000 ppm is equivalent to an outdoor concentration of 0.49 ppm, for example. The partial pressure of CO in the calibration cell for these measurements was never sufficiently high to produce significant self-broadening of the spectral lines, an effect which would yield incorrect calibration by this procedure.

IV. MONITORING RESULTS AND DISCUSSION

In this section we show examples of the capabilities of a bistatic tunable laser system for atmospheric monitoring, illustrating such features as sensitivity for ambient-air measurements, real-time recording of rapid changes in pollutant level, and the ability to perform continuous monitoring for extended periods of time.

An example of sensitive CO monitoring over the 0.61 km path is shown in Fig.C-8 for a 12-minute interval during which the laser was tuned to the P(4) absorption line. Confirmation of the calibration was obtained between 1 and 3 minutes in this test by filling the calibration cell with the appropriate mixture of CO and N_2 to produce an effective 170 ppb increase in the recorded value. The slight increase in ambient CO level between 6 and 9 minutes was caused by an automobile driven along the path. The peak-to-peak noise level within the integration time of 1 sec is no larger than the width of the recorder pen, corresponding to 5 ppb of CO in this case. In general, the sensitivity measurements can be verified by tuning the laser further into the "wing" of the absorption line so that fluctuations in the pollutant gas concentration will have a smaller influence on the sensitivity determination.

Fig. C-9 illustrates continuous monitoring over a 40-min interval during which the ambient CO level was approximately 0.4 ppm and two on-line calibrations were performed. The two calibrations corresponding to 82 and 170 ppb performed during the first ten minutes merely serve as an approximate check on the system linearity, since the outdoor fluctuations during such periods are not known. However, accurate calibration for all of the data shown was made with a retroreflector in the short-path location near the collimating mirror M-1 of Fig. C-1, thereby eliminating uncertainties from a background CO level. A small van was parked near the laser path and its engine was turned on at

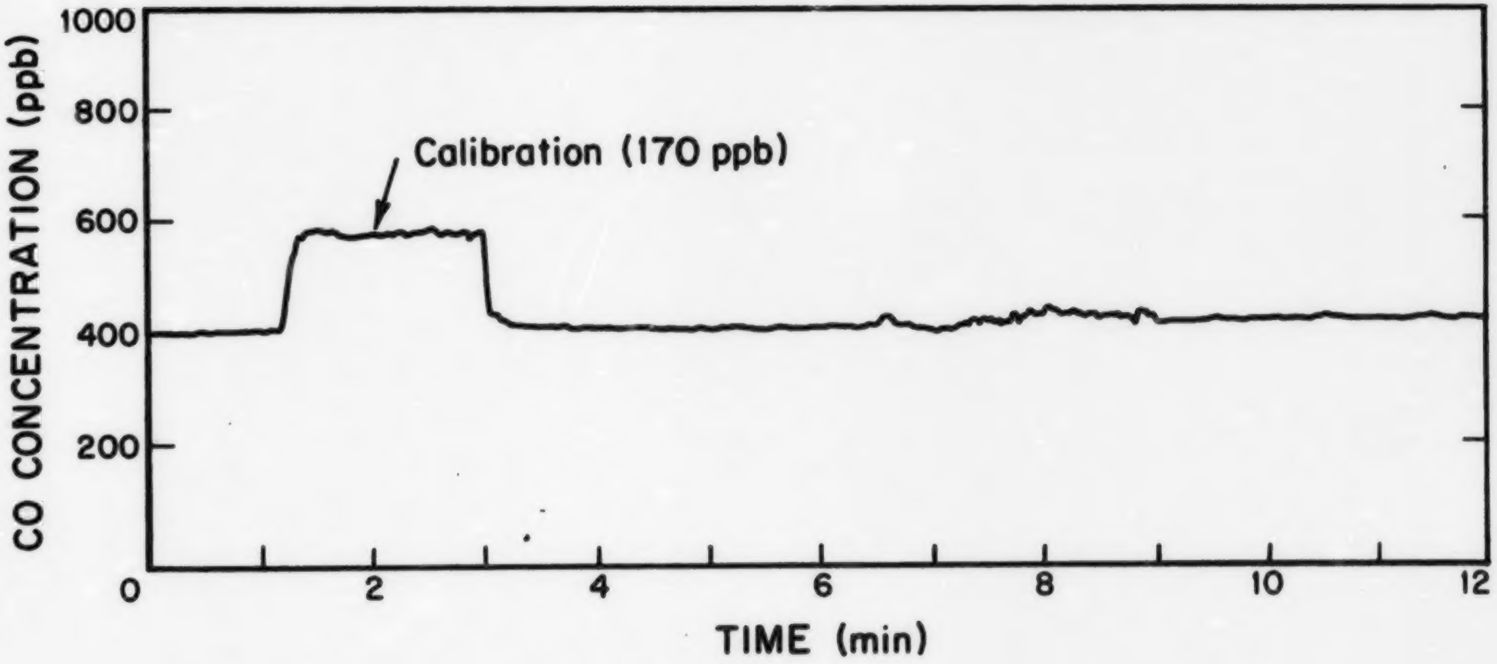

Fig.C-8. Laser monitoring of ambient CO over 0.61 km path using the P(4) line. Integration time was 1 sec.

the ten minute point for four minutes. During this period there was a slight increase in the average CO concentration along the path and in the magnitude of its fluctuations. The large initial CO emission detected when the vehicle was first started may have been caused by a rich fuel mixture, which became leaner as the engine warmed up. The source for a very noticeable increase in CO concentration at 37 minutes could not be located, but probably was a large exhaust cloud from a group of cars leaving a nearby parking lot.

Continuous measurements were performed essentially unattended for several days. The main difficulty encountered was vertical wander of the laser beam at sunrise and sunset caused by opposite temperature gradients in the atmosphere. This effect was corrected by optimizing the direct transmission signal (which was usually recorded on the strip chart with a second pen) with the elevation micrometer of the transmitting mirror. The data for Fig.C-10 were taken during early morning hours on successive days in order to observe the increase in ambient CO level resulting from commuter traffic. The dashed lines indicate periods when checks were being made of the system. A rise in CO level to 1 ppm occurred at 7:30 a.m. in Fig.C-10(a); and in Fig.C-10(b) there was a secondary increase at 8:45 a.m. as the wind changed direction and carried exhaust pollutants from Route 128, a major highway located a few miles southeast of our monitoring range. During the early morning hours (2-6 a.m.), when road traffic in the area was very light, the CO

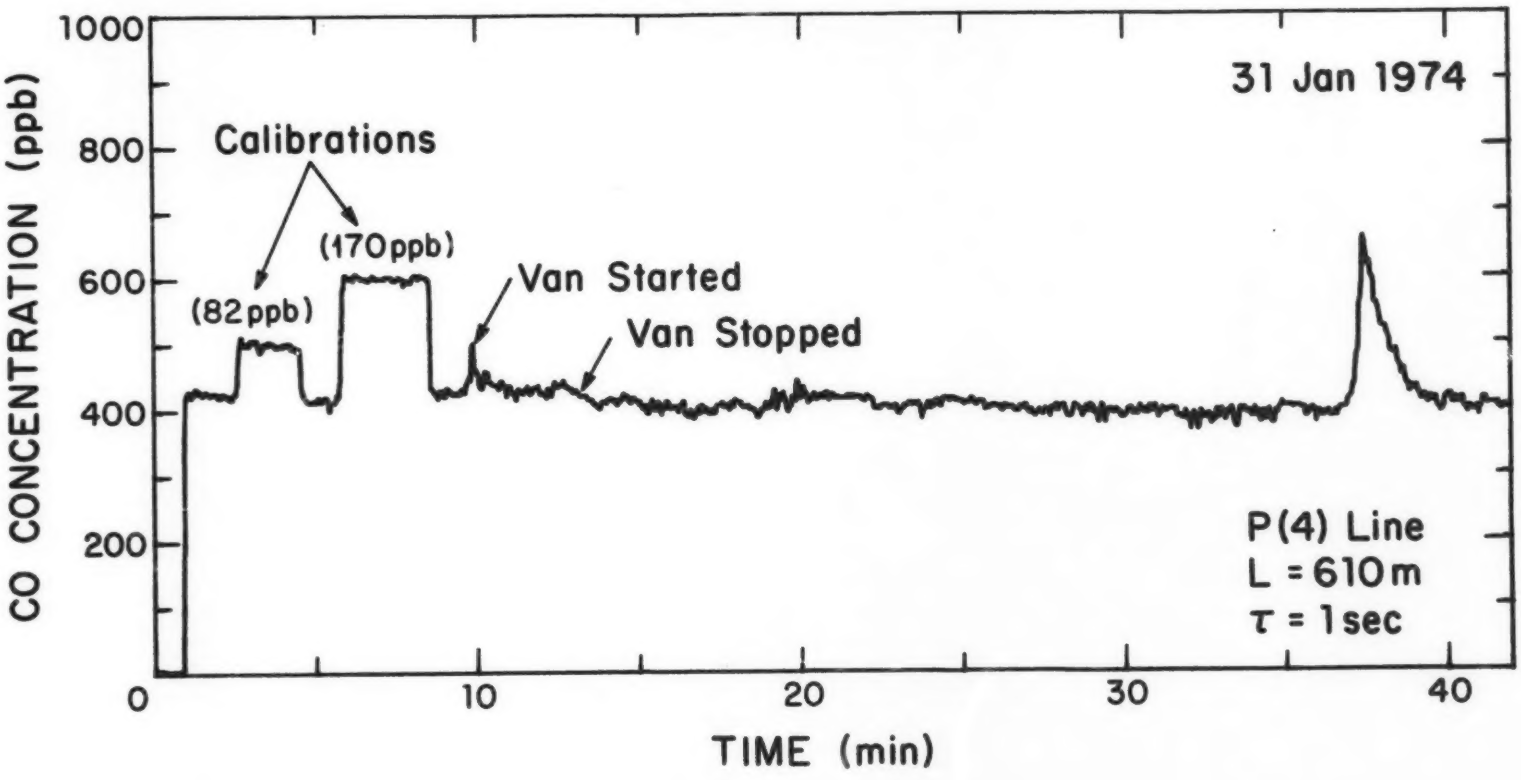

Fig.C-9. Laser monitoring of ambient CO over 0.61 km path using the P(4) line, illustrating effects caused by intentionally adding CO to a portion of the path. Integration time was 1 sec.

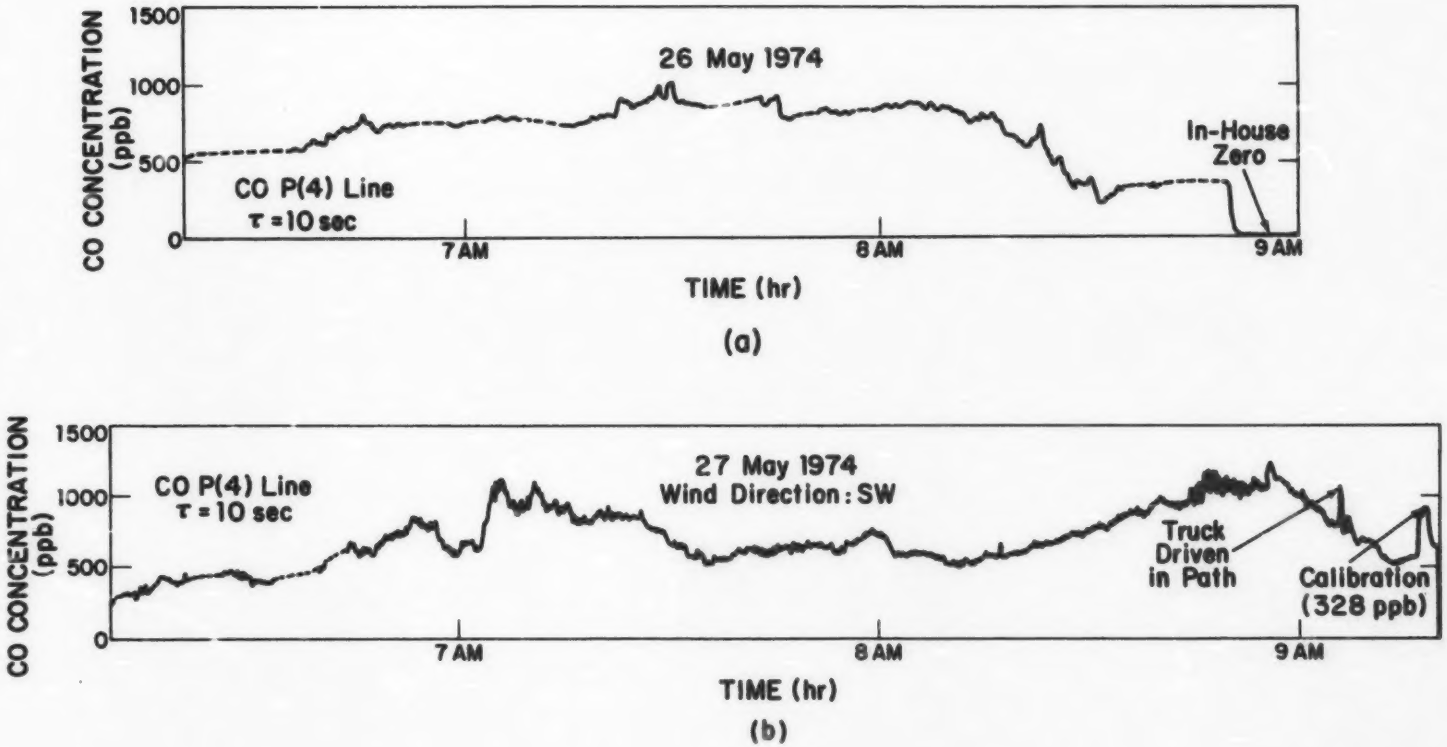

Fig.C-10. Laser monitoring of ambient CO over 0.61 km path on two successive mornings. Around 8 a.m. on 27 May 1974 the local wind direction shifted from northerly to southeasterly, carrying exhaust emissions from Route 128 into the monitoring area. The integration time was 10 sec.

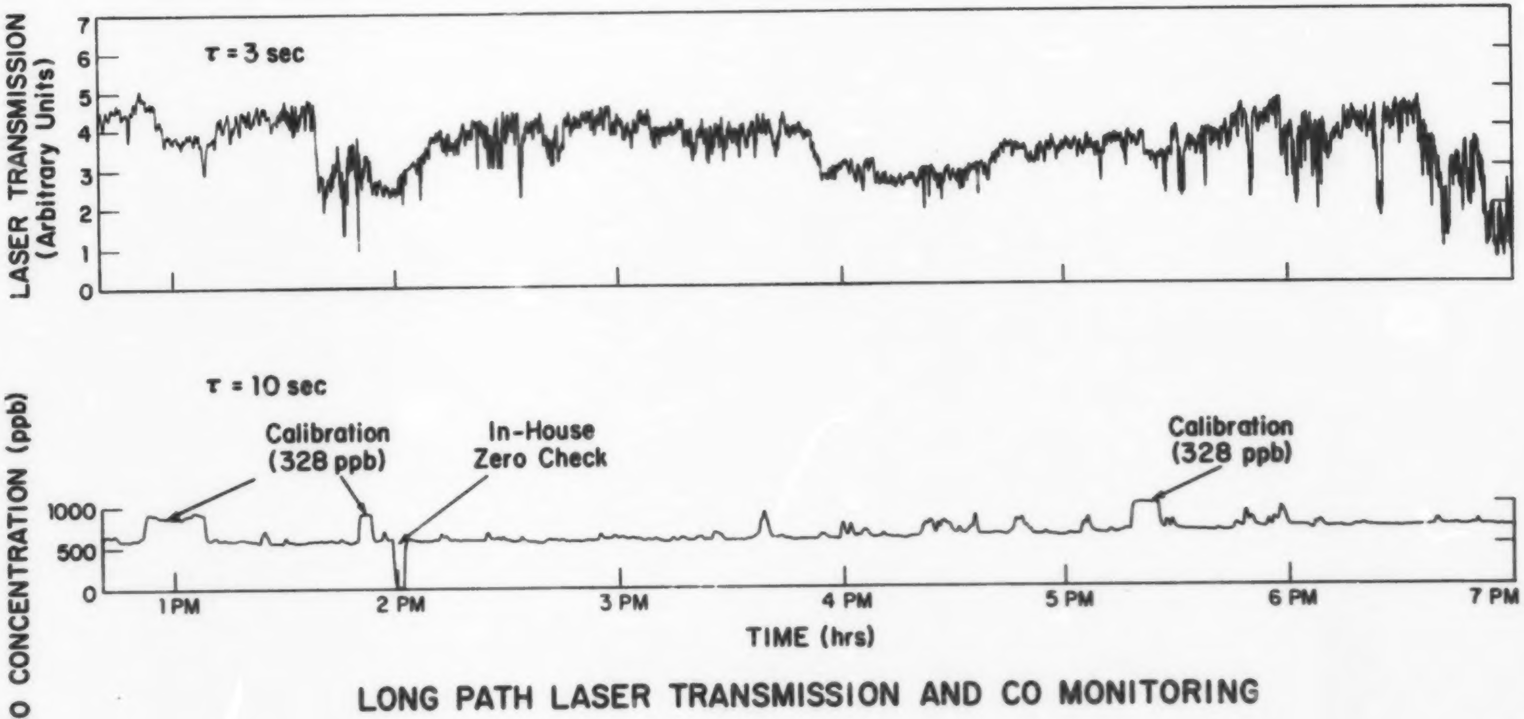

Fig.C-11. Long-path (0.61 km) monitoring of CO over an extended period of time. The upper curve is the direct transmission signal using a 3 sec time constant. The lower curve is the CO measurement using a 10 sec time constant.

concentration generally diminished to around 0.3 ppm, the background level for this location.

Fig. C-11 demonstrates the continuous, long-term capability of this laser monitoring technique, during which both the direct transmission and CO level were recorded for slightly over six hours. It should be noted that during this period there were both short-term and long-term variations in transmission, caused primarily by the $\beta(t)$ term in Eq. (1), but that these fluctuations are not reflected in the CO measurement due to the ratioing technique employed. During the period between 3:30 p.m. and 6:00 p.m. there were segments of several minutes' duration when the CO level increased by 30-40%, then returned to its original value. These variations reflect not only the pattern of vehicular traffic in the area but changes in wind direction and speed; and in order to develop regional pollutant dispersion models it is clear that such meteorological variables are extremely important.

At the time when these experiments were performed, no conventional CO point monitor having sufficient sensitivity was available for correlative measurements; however, in experiments recently completed in St. Louis such comparisons were made, and they corroborated our calibration procedure. The results of these later experiments, directed toward the application of long-path laser techniques to atmospheric monitoring and modeling, will be reported in a future article.

V. SUMMARY AND CONCLUSION

A sensitive (5 ppb) long-path laser monitoring system for CO has been developed and operated in the field. It is based on the principle of resonance absorption and employed a $PbS_{0..82}Se_{0.18}$ semiconductor diode laser mounted in a closed-cycle cryogenic cooler. A simple optical system consisting of off-axis paraboloid, remote retroreflector, and beam-splitter was used to transmit and receive the laser beam. Tests were conducted over a 0.61 km path in order to determine the average ambient CO concentration using a novel derivative technique which effectively eliminated the adverse effects of atmospheric turbulence and scattering. During these experiments it was possible to observe increases in CO level due to individual automobiles as well as the longer-term increases caused by commuter traffic. This diode laser technique can be extended to other pollutants by incorporating an additional laser for each gas or by using one of the new wide-range tunable diode lasers[24] which can monitor different pollutant gases in succession. We have assembled the present system into a mobile van for participation in the first Regional Air Pollution Study of the U. S. Environmental Protection Agency in St. Louis Missouri; and the initial experiments confirmed our calibration procedure and extended the monitoring pathlength to 2 km.

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TABLE I

DIODE LASER SPECTROSCOPIC DATA OF SEVERAL ATMOSPHERIC CO LINES

Line Designation *	Wavenumber (cm^{-1})	Linewidth (cm^{-1})	Strength (cm^{-1}/ppm)
P(1)	2139.43	0.13	1.8×10^{-5}
P(2)	2135.55	0.14	2.0
P(3)	2131.64	0.13	3.5
P(4)	2127.69	0.13	3.8
P(5)	2123.70	0.10	7.1
P(6)	2119.68	0.10	4.3
P(7)	2115.63	0.11	4.5
P(8)	2111.55	0.12	4.9

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* Refer to Fig. 2.

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